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Preparation of Titanium Fluoroalkoxides by Alcoholysis of Titanium Alkoxides

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Reaction of $Ti(OR)_4$ where R = *i*-Pr and Et with >4 equiv of fluoroalcohols, HOR^f [$R^f = CH(CF_3)_2$, C_6F_5, 2,6-$F_2C_6H_3$, 2,4-$F_2C_6H_3$, 4-FC_6H_4, C_6H_5], results in the formation of a series of $Ti(OR^f)_x(OR)_{4-x}(HOR)_n$ compounds where $x = 2-4$ and $n = 0$ or 1. Only in the cases of $R^f = CH(CF_3)_2$ ($x = 2$) and 2,6-$F_2C_6H_3$ ($x = 2$ and 3) does $n = 0$. The degree of substitution can be correlated to the electron-withdrawing ability of the R^f group, with highly electron-withdrawing groups disfavoring complete substitution. These compounds have been characterized by combustion elemental analysis and infrared and ^1H and ^{19}F NMR spectroscopies. Single-crystal X-ray diffraction studies of $Ti(OR^f)_x(OR)_{4-x}(HOR)$ [$R^f = CH(CF_3)_2$, R = Et, and $x = 2$; $R^f = C_6F_5$, R = *i*-Pr, and $x = 3$], revealed centrosymmetric dinuclear structures held together by bridging oxygen atoms. The coordination geometries approximate edge-shared bioctahedra with the coordinated alcohols hydrogen-bonding across the dinuclear unit to an oxygen atom of an alkoxide. Crystal data for $[Ti\{OCH(CF_3)_2\}_2(OEt)_2(HOEt)]_2$ at 25 °C: $a = 10.233(3)$ Å, $b = 12.702(4)$ Å, $c = 16.175(7)$ Å, $\beta = 96.05(3)°$, $Z = 2$, $d_{calc} = 1.646$ g cm^{-3}, space group $P2_1/n$, $R_F = 0.074$, and $R_{wF} = 0.076$. Crystal data for $[Ti(OC_6F_5)_3(O\text{-}i\text{-}Pr)(HO\text{-}i\text{-}Pr)]_2 \cdot C_7H_8$ at 25 °C: $a = 11.1009(9)$ Å, $b = 19.388(1)$ Å, $c = 14.397(1)$ Å, $\beta = 92.805(6)°$, $Z = 2$, $d_{calc} = 1.636$ g cm^{-3}, space group $P2_1/n$, $R_F = 0.0773$, and $R_{wF} = 0.0879$. The X-ray crystal structure of $[Ti(O\text{-}2,6\text{-}F_2C_6H_3)_3(O\text{-}i\text{-}Pr)]_2$ has also been determined. The coordination geometry defined by the oxygen atoms of the alkoxide ligands approximates a square-based pyramid, with an isopropoxide in the apical site [Ti(1)−O(4) = 1.718(6) Å and Ti(1)−O(4)−C(4) = 159.6(6)°]. One of the terminal phenoxides has a nearly linear angle [169.3(6)°], while the other has a relatively acute angle [123.3(4)°]. The phenyl group of the latter is oriented such that a fluorine fills the site trans to the isopropoxide. Ti(1)−F(1) = 2.704(5) Å is virtually identical to the sum of the van der Waals radii of fluorine and Ti(IV). Crystal data at 25 °C: $a = 11.4404(9)$ Å, $b = 18.927(2)$ Å, $c = 10.830(1)$ Å, $\beta = 114.968(7)°$, $Z = 2$, $d_{calc} = 1.541$ g cm^{-3}, space group $P2_1/c$, $R_F = 0.0564$ and $R_{wF} = 0.0573$. The two compounds that do not coordinate alcohol [R = *i*-Pr; R^f = 2,6-$F_2C_6H_3$, $x = 3$, and $R^f = CH(CF_3)_2$, $x = 2$], also do not form stable complexes with Lewis bases such as acetonitrile or THF. This contrasts with $Ti[OCH(CF_3)_2]_4$, which forms volatile $Ti[OCH(CF_3)_2]_4L_2$ [L = MeC≡N and THF] compounds. The structure of $Ti[OCH(CF_3)_2]_4(N{\equiv}CMe)_2$ has been determined using X-ray crystallography. The nitrile ligands occupy cis positions in the distorted octahedral coordination geometry. Crystal data for at 25 °C: $a = 10.2872(7)$ Å, $b = 15.295(1)$ Å, $c = 18.651(1)$ Å, $Z = 4$, $d_{calc} = 1.811$ g cm^{-3}, space group $C222_1$, $R_F = 0.0583$, and $R_{wF} = 0.0550$.

Introduction

There has been a resurgence in basic research concerning metal alkoxides due to their potential as precursors to metal oxide materials by sol−gel or chemical vapor deposition (CVD) techniques.[2−6] In addition, metal alkoxides are often useful intermediates in catalytic and stoichiometric organic transformations such as olefin and acetylene metathesis and polymerization.[6,7] We are particularly interested in metal fluoroalkoxides (OR^f), which have received a great deal of recent attention for both of these general applications. Fluoroalkoxide ligands potentially have advantages over halides or alkoxides due to a number of properties including (1) volatility,[6] (2) Lewis acidity,[8,9] (3) steric control over reactivity,[6] and (4) a reasonable degree of inertness as ancillary ligands.[10]

There are several general methods for the preparation of metal alkoxides, the most common being metathesis and alcoholysis, eqs 1 and 2.[6] Titanium(IV) alkoxides, $Ti(OR)_4$ (R = Et and *i*-Pr), have been known for several decades, most often being prepared by metathesis of $TiCl_4$. Alternatively, Winter and coworkers have noted incomplete substitutions when $TiCl_4$ was

$$MX_n + nM'OR \rightarrow M(OR)_n + nM'X \qquad (1)$$

$$X = \text{halide};\ M' = Li, Na, K, Tl, \text{etc.}$$

$$MR_n + nHOR' \rightarrow M(OR)_n + nHR \qquad (2)$$

$$R = \text{alkyl, amide, alkoxide}$$

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(2) Bradley, D. C. *Chem. Rev.* **1989,** *89,* 1317.

(3) Hubert-Pfalzgraf, L. G. *New. J. Chem.* **1987,** *11,* 663.

(4) Flaschen, S. S. *J. Am. Chem. Soc.* **1955,** *77,* 6194.

(5) Nemoto, M; Yamanaka, M. *J. Mater. Res.* **1990,** *5,* 1.

(6) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides;* Academic Press: New York, 1978.

(7) (a) Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Kruger, C.; Betz, P. *Organometallics* **1990,** *9,* 2262. (b) Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988,** *110,* 1423. (c) Schaverien, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986,** *108,* 2771. (d) Freudenberger, J. H.; Schrock, R. R.; Chuchhill, M. R.; Rheingold, A. L.; Ziller, J. W. *Organometallics* **1984,** *3,* 1563.

(8) Abbott, R. G.; Cotton, F. A.; Falvello, L. R. *Inorg. Chem.* **1990,** *29,* 514.

(9) Scholz, M.; Noltemeyer, M.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1989,** 1383.

(10) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry,* 5th ed.; Wiley & Sons: New York, 1988.

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reacted with excess 2-haloethanols. They were able to crystallographically characterize $[TiCl_2(OCH_2CH_2Cl)(HOCH_2CH_2Cl)]_2$, which adopts an edge-shared bioctahedral structure with the coordinated alcohol hydrogen-bonding across the dinuclear unit.[11] Alcohol exchange reactions have previously been noted to provide incomplete substitution products which limits the utility of this approach for the preparation of homoleptic compounds.[6]

The group IV metal hexafluoroisopropoxides were first prepared by Mazdiyasni and Schaper using the metathesis approach.[12] We have focused our attention on alternative alcoholysis routes to determine if homoleptic titanium fluoroalkoxides can be prepared by this method.[13,14] There is a general understanding of the factors that influence the degree of substitution in alcoholysis reactions, but a potential further complication for fluoroalkoxides is secondary coordination of halogen atoms.[15−24]

In this paper we present a detailed study of the alcoholysis of $Ti(OR)_4$ where R = Et and *i*-Pr using hexafluoro-2-propanol, phenol, and various fluoro-substituted phenols. A range of $Ti(OR)_{4-x}(OR^f)_x(HOR)_n$ compounds [$x = 2-4$; $n = 0$ and 1] have been prepared with varying degrees of substitution. The most novel aspect of this study is the preparation, reactivity and structural characterization of two compounds which do not coordinate the byproduct 2-propanol. We compare the Lewis acidity of these two compounds to that of $Ti[OCH(CF_3)_2]_4$.[12]

Results and Discussion

Synthesis. We have investigated the alcoholysis of $Ti(OR)_4$, where R = *i*-Pr and Et, using stoichiometric excesses (>4 equiv) of a variety of fluorinated phenols, phenol and hexafluoroisopropanol in refluxing toluene, eq 3. Our reaction conditions were chosen to favor the greatest possible extent of substitution via this alcohol exchange reaction.

There are three important factors that influence the extent of substitution in alcoholysis reactions: (1) the steric requirements of the ligands and the alcohol, (2) the relative ΔH° of ionization of the reactant and product alcohols, and (3) the relative bond strengths of the alkoxides. The driving force for substitution based on the relative gas-phase ΔH° of ionization for the reactant and product alcohols should be favorable for substitution.[25] On the other hand, the relative bond strengths of the alkoxides and fluoroalkoxides seem to be the dominant factor reflected in the results presented in eq 3. For the highly electron withdrawing groups, C_6F_5 (**2** and **8**) and $CH(CF_3)_2$ (**1** and **7**) only partial substitution is observed. Alcoholysis employing phenol (**6** and **12**) or 4-fluorophenol (**5** and **11**) readily results in complete substitution. For alcoholysis reactions involving the disubstituted phenols, the 2,6-difluorophenoxide is sufficiently electron withdrawing to prevent complete substitution (**3** and **9**) while complete substitution is observed with the 2,4-difluorophenoxide (**4** and **10**).

$$Ti(OR)_4 + {>}4HOR^f \xrightarrow[12\ h]{toluene,\ 120\ ^\circ C} Ti(OR^f)_x(OR)_{4-x}(HOR)_n + (x - n)HOR \quad (3)$$

1−12

compd	R	R^f	*x*	*n*
1	*i*-Pr	$CH(CF_3)_2$	2	0
2	*i*-Pr	C_6F_5	3	1
3	*i*-Pr	$2,6\text{-}F_2C_6H_3$	3	0
4	*i*-Pr	$2,4\text{-}F_2C_6H_3$	4	1
5	*i*-Pr	$4\text{-}FC_6H_4$	4	1
6	*i*-Pr	C_6H_5	4	1
7	Et	$CH(CF_3)_2$	2	1
8	Et	C_6F_5	3	1
9	Et	$2,6\text{-}F_2C_6H_3$	3	1
10	Et	$2,4\text{-}F_2C_6H_3$	4	1
11	Et	$4\text{-}FC_6H_4$	4	1
12	Et	C_6H_5	4	1

Alkoxides are known to be excellent ligands for the stabilization of early transition metal ions in high oxidation states.[26] This is primarily the result of metal−oxygen multiple bond formation, with the possible donation of up to three pairs of electrons per oxygen. It has been recognized that substitution of protons by fluorine in metal alkoxides reduces the ability of the oxygen atom to act as an electron donor, imparting pseudohalide character.[8] As the stepwise alcoholysis proceeds, the electrophillic metal is forced to rely to an ever increasing degree on the donation of electrons from the remaining alkoxides.[13] Alcohol exchange reactions for coordinatively unsaturated metal alkoxides are thought to occur by initial coordination of the reactant alcohol, followed by proton transfer from the reactant alcohol to an alkoxide.[6] This second step effectively reduces the metal−oxygen bond order and ultimately facilitates the dissociation of the product alcohol. If the lone pairs of an alkoxide are substantially involved in metal−oxygen π-bonding or if the coordination environment of the metal is saturated due to steric constraints the probability of further substitution is greatly reduced.

Previously we reported that reaction of $Ti(O\text{-}i\text{-}Pr)_4$ with 2 equiv of hexafluoroisopropanol produces **1**.[13] Mass spectroscopic evidence was presented for the formation of small amounts of $Ti(OR^f)_x(OR)_{4-x}$ where $x = 1$ and 3. We now know that **1** is the major product even under conditions of refluxing toluene and excess hexafluoro-2-propanol. The reaction of $Ti(OEt)_4$ with hexafluoroisopropanol also results in substitution of two alkoxides by hexafluoroisopropoxides ($x = 2$), but, in this case we observe the formation of an ethanolate (**7**). The coordination of the byproduct alcohol is presumably a reflection of the overall steric requirements of the alkoxide ligands.

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(11) Winter, C. H.; Sheridan, P. H.; Heeg, M. J. *Inorg. Chem.* **1991**, *30*, 1962.

(12) Mazdiyasni, K. S.; Schaper, B. J.; Brown, L. M. *Inorg. Chem.* **1971**, *10*, 889.

(13) Fisher, J.; Van Der Sluys, W. G.; Huffman, J. C.; Sears, J. *Synth. React. Inorg. Met.-Org. Chem.* **1993**, *23*, 479.

(14) Alcoholysis of TiR_4 [R = $CH_2\text{-}t\text{-}Bu$ and CH_2Ph] using fluoroalcohols appears to be a convenient method for the preparation of $TiR_{4-x}(ORf)_x$ [$x = 1-4$] compounds. Bott, S.; Van Der Sluys, W. G. Results to be published. See also ref 14.

(15) Samuels, J. A.; Zwanziger, J. W.; Lobkovsky, E. B.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 4046.

(16) Purdy, A. P.; George, C. F.; Callahan, J. H. *Inorg. Chem.*, **1991**, *30*, 2812.

(17) Purdy, A. P.; George, C. F. *Inorg. Chem.* **1991**, *30*, 1970.

(18) Caulton, K. G.; Hubert-Phalzgraf, L. G. *Chem. Rev.* **1990**, *90*, 969 and references therein.

(19) Kulawiec, R. J.; Crabtree, R. H. *Coord. Chem. Rev.* **1990**, *99*, 89.

(20) Witt, M.; Roesky, H. W. *Prog. Inorg. Chem.* **1992**, *40*, 353.

(21) Schluter, R. D.; Cowley, A. H.; Atwood, D. A.; Jones, R. A.; Bond, M. R.; Carrano, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 2070.

(22) Roesky, H. W.; Scholz, M.; Noltemeyer, M.; Edelman, F. T. *Inorg. Chem.* **1989**, *28*, 3829.

(23) Brooker, S.; Bertell, N.; Stalke, D.; Noltemeyer, M.; Roesky, H. W.; Sheldrick, G. M.; Edelmann, F. T. *Organometallics* **1992**, *11*, 192.

(24) Brooker, S.; Edelmann, F. T.; Kottke, T.; Roesky, H. W.; Sheldrick, G. M.; Stalke, D.; Whitmire, K. H. *J. Chem. Soc., Chem. Commun.* **1991**, 144.

(25) (a) The gas-phase ΔH°_{ion} of molecules such as alcohols generally correlates with the electron-withdrawing nature of the R groups; thus all else being equal, more electronegative substitutents increase acidities. Since $\Delta H^\circ_{ion} = D(H{-}OR) + IE(H) - EA(HOR)$, and since the ionization energy (IE) for a hydrogen atom is constant, the ΔH°_{ion} should correlate with the electron affinity (EA) of the alkoxy radical, as it does. For a complete discussion of gas phase acidities see: Jolly, W. L. *Modern Inorganic Chemistry*; McGraw-Hill: New York, 1991; pp 201−207. (b) Patai, S. *The Chemistry of the Hydroxyl Group*; Interscience Publishers: New York, 1971.

(26) King, R. H.; Chisholm, M. H.; Clark, D. L.; Hammond, C. E. *J Am. Chem. Soc.* **1989**, *111*, 2751.

Table 1. Crystal Data for **2**, **3**, **7**, and **15**

formula	$C_{55}H_{38}F_{30}O_{10}Ti_2$	$C_{42}H_{32}F_{12}O_8Ti_2$	$C_{24}H_{36}F_{24}O_{10}Ti_2$	$C_{16}H_{10}F_{24}N_2O_4Ti$
color	yellow	yellow	colorless	colorless
cryst dimens, mm	0.3 × 0.35 × 0.4	0.21 × 0.22 × 0.24	0.25 × 0.42 × 0.48	0.32 × 0.38 × 0.42
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$C222_1$
T, °C	25	25	25	25
cell dimens (25 reflcns)				
a, Å	11.1009(9)	11.4404(9)	10.233(3)	10.2872(7)
b, Å	19.388(1)	18.927(2)	12.702(4)	15.295(1)
c, Å	14.397(1)	10.830(1)	16.175(7)	18.651(1)
β, deg	92.805(6)	114.968(7)	96.05(3)	90
Z (molecules/cell)	2	2	2	4
vol, Å^3	3094.8(4)	2125.9(4)	2091(1)	2927.6(4)
d(calcd), g cm^{-3}	1.636	1.544	1.646	1.811
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73
linear abs coeff, cm^{-1}	3.95	4.71	5.24	4.62
scan speed, deg min^{-1}	0.67−8	0.67−8	0.67−8	0.67−8
scan width, deg	$0.8 + 0.35 \tan\theta$	$0.8 + 0.35 \tan\theta$	$0.8 + 0.35 \tan\theta$	$0.8 + 0.35 \tan\theta$
2θ, deg (min−max)	2−44	2−44	2−44	2−50
no. of unique intens	3927	2701	2695	2693
no. with $F_o \geq 6\,\sigma(F_o)$	2234	1299	1150	1849
R_F, R_{wF}[a]	0.0773, 0.0879	0.0564, 0.0573	0.074, 0.076	0.0583, 0.0550

[a] $R_F = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $R_{wF} = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$.

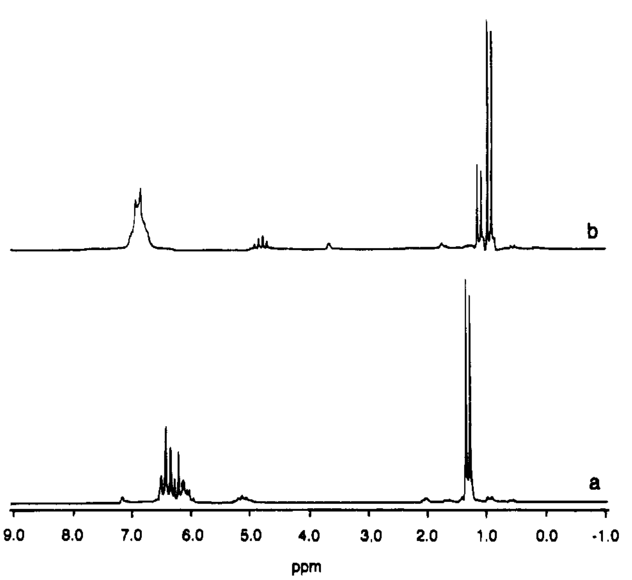

Figure 1. ^{1}H NMR spectra (90 MHz) of a 3:1 mixture of **3** and **13** in (a) benzene-d_6 and (b) THF-d_8. The ^{1}H impurity of benzene-d_6 was set at 7.15 ppm and the ^{1}H impurity of the α-CH_2 of THF-d_8 was set at 1.73 ppm.

Similarly, we observe the formation of alcoholates for the phenoxides **2** and **4**−**12**, except for **3**.

Coordination Chemistry. In order to gauge the Lewis acidity of the compounds that did not coordinate the byproduct alcohol, we investigated the reactivity of these compounds with other potential Lewis bases.

1 and **3** only loosely coordinate Lewis bases such as THF and acetonitrile (N≡CMe). Large crystals of the solvent-free compounds can be obtained by recrystallization from saturated solutions of THF or acetonitrile. We have found that ^{1}H NMR spectroscopy in THF-d_8 or acetonitrile-d_3 is a useful way to monitor the progress of the alcoholysis reactions. Figure 1 compares the ^{1}H NMR spectra of a 3:1 mixture of (**3**) and Ti(O-2,6-$F_2C_6H_3)_2$(O-*i*-Pr)$_2$ (**13**) in benzene-d_6 and THF-d_8. This ratio is easily determined by the relative integration of the isopropyl and aromatic protons and the identity of the latter was confirmed by independent preparation (see experimental). In benzene-d_6 at 30 °C and 90 MHz there is only one type of isopropyl group, presumably due to an intermolecular ligand exchange process that is faster than the NMR time-scale.[6,13] In THF-d_8 this exchange process is either completely prevented or considerably slowed by the coordination of THF. The NMR spectrum was identical to the original after the THF-d_8 was removed *in vacuo* and the solid was redissolved in benzene-d_6.

In contrast to the relatively poor Lewis acidity of **1** and **3**, addition of liquid Ti[OCH($CF_3)_2]_4$ (**14**) to acetonitrile or THF, followed by removal of the solvent *in vacuo* produced colorless crystalline solids having empirical formulas of Ti{OCH($CF_3)_2\}_4$(L)$_2$ (eq 4) where L = N≡CMe (**15**) and THF (**16**). Both **15** and **16** are hydrocarbon soluble, sublimable, and low melting (**15**, 76−80 °C; **16**, 35−39 °C) solids.

$$\mathrm{Ti\{OCH(CF_3)_2\}_4} + {>}2\mathrm{L} \xrightarrow{\mathrm{N{\equiv}CMe\ or\ THF}} \underset{\mathbf{15,\,16}}{\mathrm{Ti\{OCH(CF_3)_2\}_4(L)_2}} \quad (4)$$

$$\mathrm{L = N{\equiv}CMe}\ (\mathbf{15})\ \mathrm{and\ THF}\ (\mathbf{16})$$

The room temperature ^{1}H and ^{19}F NMR spectra of both **15** and **16** indicated that there is only one type of nondiastereotopic CH($CF_3)_2$ group. The NMR signals were somewhat broad suggesting that there is a dynamic exchange process. This process could be due to ligand rearrangement, i.e., cis to trans isomerization by dissociation of a ligand to form a five coordinate species. Unfortunately we have been unable to determine the nature of this process since both **15** and **16** precipitate from solution at low temperatures.

Solid-State and Molecular Structures. Four of the titanium fluoroalkoxide complexes prepared for this study (**2**, **3**, **7**, and **15**) have been examined by single-crystal X-ray diffraction techniques. The structure of **1** has previously been described in detail.[13] Compounds **1**, **2**, **3**, and **7** all adopt dinuclear structures, while **15** is mononuclear. A summary of data collection and crystallographic parameters for **2**, **3**, **7**, and **15** is given in Table 1. Fractional coordinates can be found in Tables 2−5 and selected bond distances and angles are provided in Tables 6−8.

Both **2** and **7** adopt centrosymmetric edge-shared bioctahedral structures (Figures 2 and 3) in which each titanium atom has a coordinated alcohol.[6,11,27] While the hydrogen atoms of the alcohols were not located, hydrogen bonding across the dinuclear unit to an alkoxide oxygen atom is indicated by the O(2)−Ti(1)−O(5) angles [163.4(3) and 167.1(4)° for **2** and **7**, respec-

---

(27) (a) Vaartstra, B. A.; Huffman, J. C.; Gradeff, P. S.; Hubert-Pfalzgraf, L.; Daran, J.-C.; Parraud, S.; Yunlu, K.; Caulton, K. G. *Inorg. Chem.* **1990**, *29*, 3126. (b) Jennings, J. S.; Wardlaw, W.; Way, W. J. *J. Chem. Soc.* **1936**, 637.

Table 2. Fractional Coordinates and Isotropic Thermal Parameters for **2**[a]

atom	x	y	z	B_{iso}, Å^2
Ti(1)	0.4964(2)	0.0567(1)	0.5918(1)	3.27(4)
O(1)	0.5743(6)	0.0384(3)	0.4680(4)	2.9(2)
O(2)	0.3605(7)	0.0972(4)	0.5286(5)	4.5(2)
O(3)	0.4262(7)	0.0356(4)	0.7009(5)	4.2(2)
O(4)	0.5767(8)	0.1300(4)	0.6191(5)	4.9(2)
O(5)	0.6365(6)	−0.0126(4)	0.6358(5)	3.8(2)
C(1)	0.6625(9)	0.0747(5)	0.4290(7)	3.2(2)*
C(2)	0.273(1)	0.1432(6)	0.5432(8)	4.4(3)*
C(3)	0.395(1)	0.0521(6)	0.7870(7)	4.0(2)*
C(4)	0.625(2)	0.199(1)	0.638(1)	12.0(6)*
C(5)	0.690(1)	−0.0311(7)	0.7265(9)	5.4(3)*
C(6a)	0.729(4)	0.198(2)	0.625(3)	11(1)*
C(6)	0.676(2)	0.208(1)	0.735(2)	5.0(6)*
C(7a)	0.637(3)	0.237(2)	0.563(2)	8.2(9)*
C(7)	0.550(3)	0.255(2)	0.595(2)	8.7(9)*
C(8)	0.743(2)	0.028(1)	0.773(1)	9.3(5)*
C(9)	0.771(1)	−0.0910(8)	0.719(1)	7.1(4)*
C(10)	0.637(1)	0.1240(6)	0.3629(8)	4.1(2)*
C(11)	0.726(1)	0.1599(6)	0.3196(8)	4.7(3)*
C(12)	0.843(1)	0.1467(7)	0.3426(9)	5.5(3)*
C(13)	0.873(1)	0.0995(6)	0.4091(8)	4.7(3)*
C(14)	0.784(1)	0.0643(6)	0.4524(7)	3.9(2)*
C(15)	0.369(1)	0.1192(6)	0.8126(8)	4.4(3)*
C(16)	0.337(1)	0.1363(7)	0.9012(9)	5.3(3)*
C(17)	0.333(1)	0.0851(7)	0.9670(9)	5.3(3)*
C(18)	0.360(1)	0.0185(7)	0.9460(8)	5.0(3)*
C(19)	0.389(1)	0.0026(6)	0.8563(8)	4.3(3)*
C(20)	0.270(1)	0.2053(8)	0.497(1)	6.8(4)*
C(21)	0.174(1)	0.2550(8)	0.510(1)	7.4(4)*
C(22)	0.093(1)	0.2370(9)	0.565(1)	7.7(4)*
C(23)	0.086(2)	0.1792(9)	0.612(1)	8.1(4)*
C(24)	0.182(1)	0.1305(7)	0.5994(9)	6.0(3)*
F(1)	0.5224(6)	0.1378(3)	0.3382(5)	5.7(2)
F(2)	0.6954(8)	0.2062(4)	0.2531(6)	8.3(2)
F(3)	0.9319(7)	0.1809(4)	0.3001(6)	8.3(2)
F(4)	0.9890(6)	0.0868(5)	0.4339(6)	7.4(2)
F(5)	0.8184(6)	0.0176(4)	0.5160(5)	5.7(2)
F(6)	0.3728(7)	0.1689(4)	0.7483(5)	6.5(2)
F(7)	0.3115(9)	0.2016(4)	0.9216(5)	8.2(2)
F(8)	0.3015(9)	0.1024(5)	1.0536(5)	8.3(2)
F(9)	0.3536(8)	−0.0307(4)	1.0088(5)	7.3(2)
F(10)	0.4133(7)	−0.0631(4)	0.8365(5)	6.2(2)
F(11)	0.3540(9)	0.2211(4)	0.4394(6)	9.4(3)
F(12)	0.180(1)	0.3123(5)	0.4603(9)	14.5(4)
F(13)	0.0002(9)	0.2851(5)	0.5796(9)	15.2(4)
F(14)	0.0030(9)	0.1633(7)	0.6707(8)	12.9(4)
F(15)	0.1759(7)	0.0716(5)	0.6469(6)	7.9(2)

[a] Starred values are for atoms that were refined isotropically. Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)\ [a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma B(1,2) + ac(\cos \beta)B(1,3) + bc\ (\cos \alpha)B(2,3)]$.

Table 3. Fractional Coordinates and Isotropic Thermal Parameters for **3**[a]

atom	x	y	z	B_{iso}, Å^2
Ti(1)	0.6379(1)	0.04028(9)	0.1014(1)	2.74(3)
O(1)	0.5491(5)	−0.0551(3)	0.0387(5)	2.9(1)
O(2)	0.7531(5)	−0.0007(3)	0.2547(5)	3.9(2)
O(3)	0.6393(5)	0.1297(3)	0.1747(5)	3.5(1)
O(4)	0.7189(5)	0.0568(3)	0.0022(5)	4.2(2)
C(1)	0.6068(7)	−0.1184(4)	0.0920(8)	3.0(2)*
C(2)	0.8338(7)	−0.0421(5)	0.3544(7)	3.3(2)*
C(3)	0.6191(8)	0.1449(5)	0.2852(8)	3.3(2)*
C(4)	0.819(1)	0.0563(7)	−0.042(1)	7.5(3)*
C(5)	0.5884(8)	−0.1495(5)	0.1962(9)	3.9(2)*
C(6)	0.6492(9)	−0.2135(6)	0.256(1)	5.6(3)*
C(7)	0.728(1)	−0.2438(6)	0.209(1)	5.8(3)*
C(8)	0.7606(9)	−0.2152(6)	0.107(1)	5.7(3)*
C(9)	0.6883(8)	−0.1520(5)	0.0498(9)	4.0(2)*
C(10)	0.780(1)	0.0383(8)	−0.178(1)	8.3(3)*
C(11)	0.8222(8)	−0.0535(6)	0.4718(9)	4.7(2)*
C(12)	0.9038(9)	−0.0972(6)	0.574(1)	5.4(2)*
C(13)	1.002(1)	−0.1287(6)	0.557(1)	6.2(3)*
C(14)	1.018(1)	−0.1207(6)	0.441(1)	6.4(3)*
C(15)	0.9336(9)	−0.0763(5)	0.3414(9)	4.7(2)*
C(16)	0.915(1)	0.1112(7)	0.026(1)	6.7(3)*
C(17)	0.5507(8)	0.1013(5)	0.3310(8)	3.8(2)*
C(18)	0.5285(9)	0.1154(6)	0.445(1)	5.2(2)*
C(19)	0.5807(9)	0.1775(6)	0.516(1)	5.5(3)*
C(20)	0.6483(9)	0.2221(6)	0.475(1)	5.2(2)*
C(21)	0.6683(8)	0.2068(5)	0.3611(8)	3.7(2)*
F(1)	0.5071(5)	0.0411(3)	0.2590(5)	5.0(1)
F(2)	0.5121(5)	−0.1184(3)	0.2442(5)	6.5(2)
F(3)	0.7258(5)	−0.0221(3)	0.4899(5)	7.4(2)
F(4)	0.9478(5)	−0.0666(3)	0.2255(5)	7.3(2)
F(5)	0.7091(5)	−0.1226(3)	−0.0531(5)	6.4(2)
F(6)	0.7382(5)	0.2496(3)	0.3199(5)	5.5(2)

[a] Starred values are for atoms that were refined isotropically. Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

tively]. The alcohol is also readily identified by the Ti(1)−O(5) bond distances [2.128(7) and 2.187(9) Å for **2** and **7**, respectively], which are longer than the corresponding distances for the alkoxides and approximate Ti−O single bonds.[11] The unit cell of **2** also includes one disordered toluene of solvation per dimer. The dinuclear unit of **7** is held together by bridging oxygen atoms of ethoxides [Ti(1)−O(1) = 2.001(7) Å and Ti(1)′−O(1) = 2.031(7) Å], whereas the dinuclear unit for (**2**) is held together by the oxygen atoms of pentafluorophenoxides [Ti(1)−O(1) = 2.050(7) Å and Ti(1)′−O(1) = 2.164(7) Å]. For both **2** and **7** there are terminal alkoxides that have relatively short Ti(1)−O(4) bond distances [1.714(8) and 1.723(8) Å, respectively] and large Ti(1)−O(4)−C(4) angles [170(1) and 170(1)°]. This is normally taken as a reflection of the π-donation of both oxygen lone pairs to the titanium atoms.[11,26]

Both **1** and **3** adopt dinuclear structures lacking coordinated alcohol (Figures 4 and 5). The coordination geometry about the titanium atoms in **1** is best described as distorted trigonal bipyramidal (TBP). The dinuclear unit is held together by bridging isopropoxides [Ti(1)−O(1) = 1.900(1) Å and Ti(1)′−O(1) = 2.121(1) Å] and there is again one terminal isopropoxide per titanium with a short Ti(1)−O(4) distance [1.752(1) Å] and an obtuse Ti(1)−O(4)−C(4) angle [175.3(1)°]. The terminal isopropoxide ligands occupy axial positions in the TBP opposite to the long bridging Ti(1)−O(1) distance and the hexafluoroisopropoxides occupy the equatorial positions of the TBP. This overall structure is reminiscent of the structure of $[TiCl_2(OC_6H_5)_2]_2$.[6]

Crystals of **3** grown from concentrated toluene or toluene/2-propanol solutions were invariably thin plates of poor quality for X-ray diffraction studies. However, we were able to collect a data set on a crystal which was obtained by slowly cooling (80−25 °C) a saturated toluene-d_8 solution. In contrast to **1**, **3** adopts a structure in which the coordination geometry defined by the oxygen atoms of the alkoxides is a distorted square-based pyramid (SBP). In this case there are bridging phenoxides [Ti(1)−O(1) = 2.043(5) Å and Ti(1)′−O(1) = 2.054(5) Å] and the terminal isopropoxide [Ti(1)−O(4) = 1.718(6) Å and Ti(1)−O(4)−C(4) = 159.6(6)°] occupies the apical site of the SBP. There are two types of terminal phenoxides, one with an obtuse Ti(1)−O(2)−C(2) angle [169.3(6)°] and one with a somewhat more acute Ti(1)−O(3)−C(3) angle [126.8(5)°]. The phenyl group of the phenoxide with the acute angle is oriented such that a fluorine atom is oriented toward the titanium [Ti(1)−F(1) = 2.704(5) Å], in the site that would potentially complete a distorted octahedral coordination geometry. This weak fluorine interaction is trans to the terminal isopropoxide which has the shortest Ti−O distance.

In general the Ti−O bond lengths of the fluoroalkoxide ligands are longer than the corresponding distances for alkox-

Table 4. Fractional Coordinates for **7**[a]

atom	x	y	z	B_{iso}, Å^2
Ti(1)	0.0432(2)	0.8871(2)	0.9646(1)	3.59(4)
O(1)	0.1135(7)	1.0199(6)	1.0191(4)	3.1(2)*
O(2)	0.0556(8)	0.9529(7)	0.8607(5)	4.6(2)*
O(3)	−0.0684(7)	0.7772(6)	0.9291(5)	4.1(2)*
O(4)	0.1875(8)	0.8162(7)	0.9746(5)	4.7(2)*
O(5)	0.0130(8)	0.8457(7)	1.0925(5)	4.9(2)*
C(1)	0.252(2)	1.052(1)	1.026(1)	8.6(5)*
C(2)	0.104(1)	0.911(1)	0.7879(8)	5.5(3)*
C(3)	−0.072(2)	0.670(1)	0.932(1)	6.9(4)*
C(4)	0.319(2)	0.767(2)	0.996(1)	12.7(7)*
C(5)	0.093(2)	0.777(2)	1.147(1)	9.1(5)*
C(6)	0.305(2)	1.035(2)	1.104(1)	12.4(7)*
C(7)	0.350(3)	0.698(2)	0.946(2)	17(1)*
C(8)	−0.187(2)	0.633(2)	0.967(1)	9.1(5)*
C(9)	0.220(2)	0.976(1)	0.768(1)	7.5(4)*
C(10)	−0.002(2)	0.912(1)	0.716(1)	8.4(5)*
C(11)	−0.054(2)	0.619(1)	0.853(1)	8.6(5)*
C(12)	0.030(2)	0.737(2)	1.215(1)	9.6(5)*
F(1)	−0.297(1)	0.6612(9)	0.9218(8)	11.8(4)
F(2)	−0.202(1)	0.672(1)	1.0406(7)	13.8(4)
F(3)	−0.200(1)	0.5286(9)	0.971(1)	16.8(5)
F(4)	−0.046(1)	0.5167(8)	0.855(1)	16.8(5)
F(5)	−0.150(1)	0.642(1)	0.7939(7)	13.2(4)
F(6)	0.051(1)	0.6532(8)	0.8205(7)	12.7(4)
F(7)	0.3185(9)	0.958(1)	0.8274(6)	10.6(3)
F(8)	0.262(1)	0.948(1)	0.6984(6)	12.1(4)
F(9)	0.203(1)	1.0769(8)	0.7683(7)	11.4(3)
F(10)	−0.109(1)	0.866(1)	0.7345(6)	12.1(4)
F(11)	−0.040(1)	1.007(1)	0.6944(8)	14.3(4)
F(12)	0.033(1)	0.865(1)	0.6509(6)	16.3(5)

[a] Starred values are for atoms that were refined isotropically. Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)\{a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 5. Fractional Coordinates for **15**[a]

atom	x	y	z	B_{iso}, Å^2
Ti(1)	0.000	0.13231(9)	0.750	3.85(2)
O(2)	0.1257(4)	0.0582(3)	0.7853(2)	4.96(9)
O(3)	0.0735(4)	0.1478(3)	0.6605(2)	4.69(9)
N(4)	0.1200(6)	0.2475(3)	0.7824(3)	6.2(1)
C(5)	0.1703(9)	0.3027(6)	0.8077(4)	8.8(2)
C(6)	0.232(1)	0.3805(7)	0.8436(6)	16.8(3)
C(7)	0.1733(6)	0.0397(4)	0.8518(4)	5.2(1)
C(8)	0.1331(9)	−0.0498(6)	0.8755(5)	8.3(2)
C(9)	0.3173(7)	0.0526(6)	0.8549(4)	8.8(2)
C(10)	0.1560(7)	0.1949(4)	0.6194(3)	5.3(2)
C(11)	0.095(1)	0.2179(6)	0.5503(4)	9.5(3)
C(12)	0.2814(9)	0.1501(7)	0.6091(5)	11.3(3)
F(13)	0.0051(6)	−0.0522(3)	0.8796(3)	13.8(2)
F(14)	0.1682(7)	−0.1109(3)	0.8293(3)	13.5(2)
F(15)	0.1752(6)	−0.0732(4)	0.9382(3)	12.6(2)
F(16)	0.3561(5)	0.1273(4)	0.8335(4)	14.3(2)
F(18)	0.3686(5)	0.0341(5)	0.9173(3)	13.2(2)
F(19)	0.3775(5)	−0.0017(5)	0.8071(3)	13.6(2)
F(20)	0.1733(6)	0.2637(4)	0.5063(3)	11.9(2)
F(21)	0.0535(8)	0.1566(5)	0.5152(3)	21.8(2)
F(22)	0.0006(8)	0.2725(5)	0.5633(3)	21.4(2)
F(23)	0.3672(6)	0.1935(5)	0.5708(3)	16.5(2)
F(24)	0.3305(6)	0.1254(6)	0.6696(4)	23.0(3)
F(25)	0.2631(9)	0.0775(4)	0.5727(5)	23.1(3)

[a] Values for anistropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

ides. For the terminal ligands the difference is approximately 0.1 Å, but can be as large as 0.18 Å.[8] This has been explained in terms of the electron-withdrawing character of the fluoroalkoxides, resulting in reduced Ti−O multiple bond character. It is also interesting to note the trans influence of the terminal alkoxides. In each case the shortest Ti−O distances are opposite or trans to the longest metal ligand interactions in **1**−**3** and **7**.

Table 6. Selected Bond Distances (Å) for Compounds **1**, **2**, **3**, and **7**[a]

	1	**2**	**3**	**7**
Ti(1)−O(1)	1.900(1)	2.050(7)	2.043(5)	2.001(7)
Ti(1)′−O(1)	2.121(1)	2.164(7)	2.054(5)	2.031(7)
Ti(1)−O(2)	1.849(1)	1.894(8)	1.802(5)	1.894(8)
Ti(1)−O(3)	1.835(1)	1.833(7)	1.867(6)	1.856(8)
Ti(1)−O(4)	1.752(1)	1.714(8)	1.718(6)	1.723(8)
Ti(1)−O(5)		2.128(7)		2.187(9)
Ti(1)−F(1)			2.704(5)	

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 7. Selected Bond Angles (deg) for Compounds **1**, **2**, **3**, and **7**[a]

	1	**2**	**3**	**7**
Ti(1)−O(1)−Ti(1)′	106.9(1)	109.5(1)	110.0(1)	107.2(2)
Ti(1)−O(1)−C(1)	118.7(1)	122.3(6)	123.3(4)	124.5(8)
Ti(1)−O(2)−C(2)	136.7(1)	140.0(7)	169.3(6)	128.9(8)
Ti(1)−O(3)−C(3)	141.5(1)	151.4(7)	126.8(5)	139.4(8)
Ti(1)−O(4)−C(4)	175.3(1)	170(1)	159.6(6)	170(1)
Ti(1)−O(5)−C(5)		133.1(7)		127.0(9)
O(1)−Ti(1)−O(1)′	73.1(1)	70.5(3)	70.0(2)	72.8(3)
O(1)−Ti(1)−O(2)	84.3(1)	90.8(3)	89.6(2)	87.9(3)
O(1)−Ti(1)−O(3)	119.1(1)	157.2(3)	148.9(3)	162.0(3)
O(1)−Ti(1)−O(4)	99.8(1)	96.1(3)	106.1(3)	97.7(3)
O(1)−Ti(1)−O(5)		79.4(3)		82.3(3)
O(4)−Ti(1)−O(5)		95.2(3)		89.5(4)
O(2)−Ti(1)−O(5)		163.4(3)		167.1(4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 8. Selected Bond Distances (Å) and Angles (deg) for **15**[a]

Bond Distances			
Ti(1)−O(2)	1.840(4)	Ti(1)−O(3)	1.848(4)
Ti(1)−N(4)	2.230(6)	O(2)−C(7)	1.363(8)
O(3)−C(10)	1.351(8)	N(4)−C(5)	1.10(1)
Bond Angles			
O(2)−Ti(1)−O(2)′	104.1(2)	O(2)−Ti(1)−O(3)	96.5(2)
O(2)−Ti(1)−N(4)	89.9(2)	O(2)−Ti(1)−N(4)′	166.0(2)
O(3)−Ti(1)−O(3)′	165.3(2)	O(3)−Ti(1)−N(4)	85.2(2)
O(3)−Ti(1)−N(4)′	83.2(2)	N(4)−Ti(1)−N(4)′	76.1(2)
Ti(1)−O(2)−C(7)	134.8(4)	Ti(1)−O(3)−C(10)	146.9(4)
Ti(1)−N(4)−C(5)	169.6(6)	N(4)−C(5)−C(6)	177(1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

We have also structurally characterized **15**, Figure 6. The orthorhombic unit cell consists of discrete mononuclear units. The coordination geometry approximates a distorted octahedron with the acetonitriles in cis positions.[10,28] The crystallographically imposed symmetry results in one type of nitrile and two types of alkoxides. The average Ti−O distance of 1.844(4) Å is within the range of the Ti−O distances [1.833(7)−1.894(8) Å] for the terminal fluoroakoxides in **1**−**3** and **7**. The Ti(1)−N(4) distance of 2.230(6) Å is slightly longer than the Ti(1)−O(5) distances [2.128(7) and 2.187(9) Å] of the coordinated alcohols in **2** and **7** and the Ti−N distances [2.160(9) and 2.172(3) Å] observed in the *fac*-$TiCl_3(N{\equiv}CMe)_3$ cation.[29]

Coordination of Alcohol. It is perhaps interesting to speculate if secondary fluorine interactions can substantially affect Lewis acidities. This question is raised by the fact that **2** forms an alcoholate while **3** does not.

The titanium−fluorine interaction observed in (**3**) is long [2.704(5) Å] compared to the known Ti−F distances of titanium

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(28) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: New York, 1984.

(29) Claire, P. P. K.; Willey, G. R.; Drew, M. G. B. *J. Chem. Soc., Chem. Commun.* **1987**, 1100.

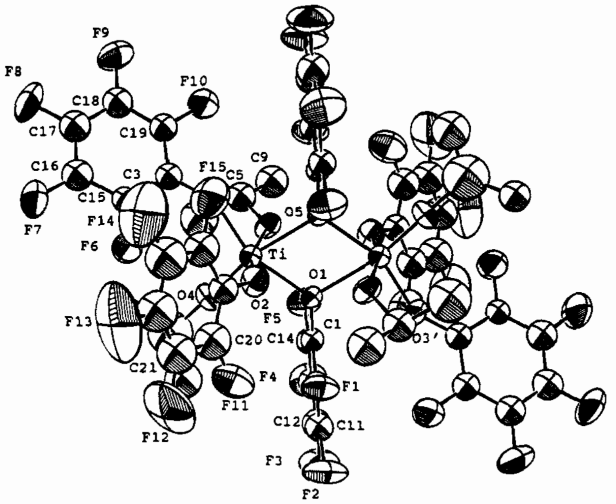

Figure 2. ORTEP drawing of **2**. Fluorines, hydrogens, and methyl carbons have been omitted for clarity to emphasize the edge-shared bioctahedral coordination geometry.

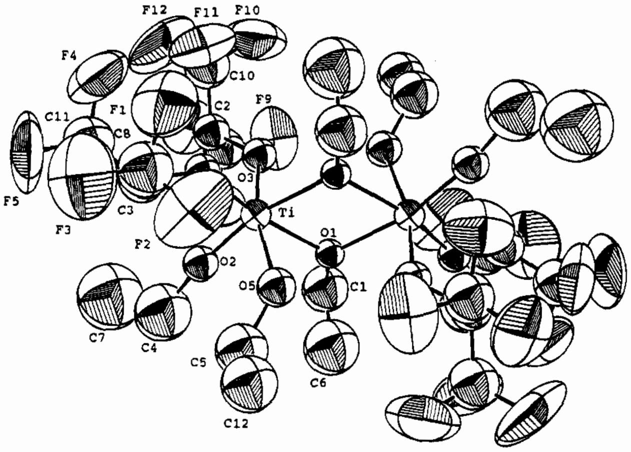

Figure 3. ORTEP drawing of **7**. Fluorines and hydrogens have been omitted for clarity to emphasize the edge-shared bioctahedral coordination geometry.

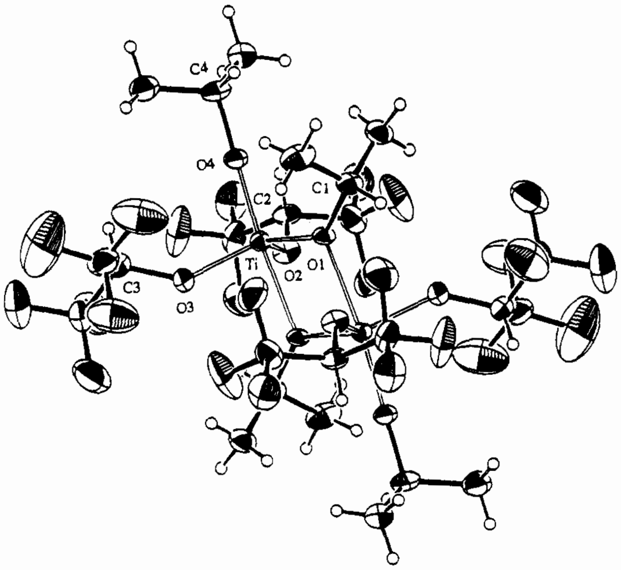

Figure 4. ORTEP drawing of **1**. Trifluoromethyl groups and hydrogens have been omitted for clarity to emphasize the edge-shared trigonal bipyramidal coordination geometry.

fluorides[28] and longer than the sum of the covalent radii of titanium and fluorine and is virtually the same as the sum of the van der Waals radii of fluorine and octahedral Ti(IV) [1.35 + 1.36 Å = 2.71 Å].[30] There have been a number of transition

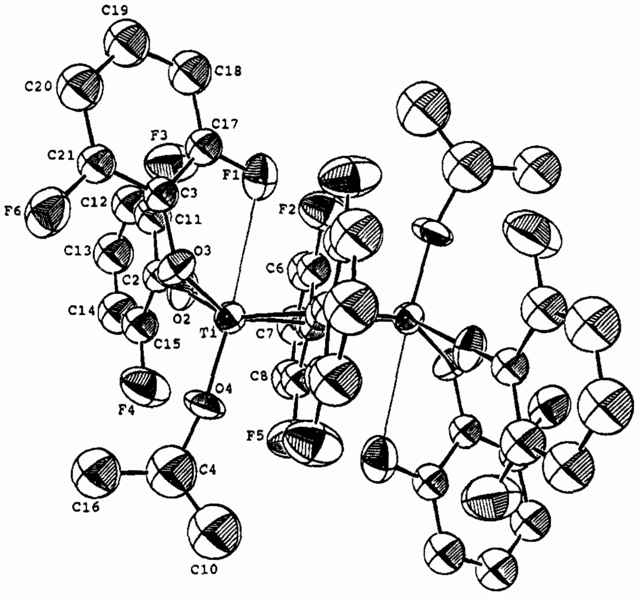

Figure 5. ORTEP drawing of **3**. Hydrogens have been omitted for clarity to emphasize the base-shared square-based bipyramidal coordination geometry and the weak titanium fluorine interaction.

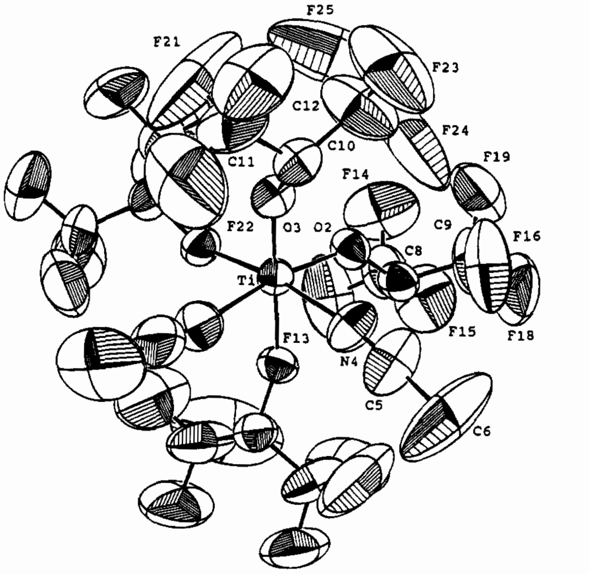

Figure 6. ORTEP drawing of **15**. Fluorines and hydrogens have been omitted for clarity to emphasize the distorted octahedral coordination geometry.

metal complexes that are thought to have weak intramolecular secondary coordination of fluorine atoms.[31-33] It is possible that the orientation of the phenoxide is merely a result of crystal packing forces and does not result from any significant Ti−F bonding interaction. We note that the M−O−C angles of terminal alkoxides in edge-shared bioctahedral structures are usually >150°.[11,27,34] In fact the other terminal 2,6-difluorophenoxide in **3** has a nearly linear Ti(1)−O(4)−C(4) angle, presumably optimizing any Ti−O π-bonding interactions. The loss of stabilization energy from bending the Ti(1)−O(3)−C(3) angle must be compensated by either, or perhaps both, the

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(30) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(31) Catala, R. M.; Cruz-Garritz, D.; Hills, A.; Hughes, D. L.; Richards, R. L.; Sosa, P.; Torrens, H. *J. Chem. Soc., Chem. Commun.* **1987**, 261.

(32) Thompson, J. S.; Sorrell, T.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4193.

(33) Kulawiec, R. J.; Holt, E. M.; Lavin, M.; Crabtree, R. H. *Inorg. Chem.* **1987**, *26*, 2559.

(34) Svetich, G. W.; Voge, A. A. *Acta Crystallogr.* **1972**, *B28*, 1760.-

packing forces or the stabilization acquired from a titanium fluorine interaction. A further sacrifice in Ti−O multiple bonding to provide an optimal Ti−O−C angle for a Ti−F interaction would presumably be energetically costly.

The Ti−O bond distances of the coordinated alcohols in **2** and **7** are intermediate between the distances exhibited by [TiCl$_2$(OCH$_2$CH$_2$Cl)$_2$(HOCH$_2$CH$_2$Cl)][11] and [Ti(OPh)$_4$(HOPh)]$_2$[34] of 2.202(4) and 2.200(11) Å, respectively. These distances are all somewhat longer than the Ti−O single bond length of 2.08 Å predicted on the basis of the sum of the covalent radii of oxygen and titanium.[30] While this suggests a weak bonding interaction, it is substantially reinforced by hydrogen bonding. How could a poor nucleophile such as a fluorine prevent the coordination of an alcohol? In the case of ethanol it does not. Obviously the steric requirements of the alcohol and alkoxides are a factor. We assume that the pentafluorophenoxide and 2,6-difluorophenoxide ligands are approximately equivalent sterically. On the other hand, the electron-withdrawing nature of these ligands is substantially different with the former making the titanium much more electrophillic. The electron-withdrawing nature of the pentafluorophenoxide can tip the scale in favor of coordination of alcohol.

Concluding Remarks

We have been able to prepare a series of Ti(OR)$_{4-x}$(OR^f)$_x$(HOR)$_n$ compounds [x = 2−4; n = 0 and 1] by the alcoholysis of titanium(IV) ethoxide and isopropoxide. The two alcoholates (**2** and **7**) that we have structurally characterized adopt the typical dinuclear edge-shared bioctahedral structure observed for a number of TiX$_4$(HOR) (X = halide or alkoxide) complexes.[6,10] On the other hand, the structures of the two compounds that do not form alcoholates (**1** and **3**) are not common structures for titanium(IV) alkoxides.[6] The structure of **3** is interesting due to the unique orientation of the phenyl group to provide a close interaction of a fluorine with titanium. This is particularly significant in light of recent reports on the activation of C−F bonds by transition metal complexes.[35]

Completely replacing alkoxides with fluorinated alkoxides, as in **14**, has a dramatic effect on the Lewis acidity of the metal ion. The increased Lewis acidity of **14** as compared to **1** is most likely the result of the paucity of electron density at the titanium and is not due to steric factors. The introduction of alkoxide ligands into the coordination environment of the titanium clearly reduces Lewis acidity due to enhanced Ti−O multiple bonding. Additionally, this increased multiple bond character obviates further substitution of alkoxides for fluoroalkoxides by alcoholysis.

Finally, this work demonstrates that the Lewis acidity of early transition metal alkoxides can be tuned by controlling (1) the electron-withdrawing nature of the alkyl group and (2) the ratio of highly electron-withdrawing alkoxides to electron-donating alkoxides. By coupling these two properties, it should be possible to achieve any desired degree of Lewis acidity.

Experimental Section

Physical Techniques. ^{1}H NMR spectra were recorded at 30 °C on either a JEOL FX90Q spectrometer at 89.56 MHz or a GE QE Plus spectrometer at 300 MHz, in dry and oxygen-free benzene-d_6 or toluene-d_8. All ^{1}H NMR chemical shifts are reported in ppm (δ) relative to an external standard of TMS (0.0 ppm) in CDCl$_3$. ^{19}F NMR spectra were obtained using the JEOL FX90Q spectrometer at 84.26 MHz and referenced to an external standard of F$_3$CCO$_2$H in D$_2$O set at 0.0 ppm.[36] Variable-temperature ^{19}F NMR spectra were recorded using a spectrometer frequency of 282 MHz. Infrared spectra were recorded on a Perkin-Elmer 1430 ratio recording infrared spectrophotometer interfaced with a Perkin-Elmer IR data station, as Nujol mulls that were prepared in the glovebox and sandwiched between NaCl salt plates. Spectra were referenced to the 1601 cm^{-1} absorption of polystyrene. Combustion elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, NY. Elemental analysis samples were handled using standard inert atmosphere techniques.

General Synthetic Procedures. All reactions were carried out in a Braun glovebox with a high capacity purification system under a helium atmosphere (≤ 1 ppm of O$_2$) or using standard Schlenk techniques. Solvents were distilled under argon from dark blue Na/benzophenone solutions and stored in the glovebox. Phenols and hexafluoro-2-propanol were purchased from Aldrich. The solids were used as received and the liquids were degassed by freeze−pump−thaw cycles.

Ti(O-*i*-Pr)$_2$[OCH(CF$_3$)$_2$]$_2$ (1). The title compound was prepared using a slight variation of the published procedure.[13] A mixture of 2.0 mL of Ti(O-*i*-Pr)$_4$, 20 mL of toluene, and a large excess of HOCH(CF$_3$)$_3$ (*ca.* 20 mL) was refluxed for 12 h. After the solvent was removed *in vacuo*, the pure product was obtained as a colorless crystalline solid by sublimation at 60−70 °C under a static vacuum using an air-cooled sublimation tube.

IR (cm^{-1}): 1371 (vs), 1338 (ms), 1289 (vs), 1265 (s), 1215 (vs), 1188 (vs), 1151 (vs), 1105 (vs), 1011 (s), 925 (ms), 894 (ms), 855 (s), 828 (ms), 761 (s), 711 (m), 687 (ms), 605 (ms), 593 (m), 587 (m), 480 (s).

Ti(OC$_6$F$_5$)$_3$(O-*i*-Pr)(HO-*i*-Pr) (2). In the glovebox, 2.60 g (14.1 mmol) of HOC$_6$F$_5$ was dissolved in *ca.* 20 mL of toluene in a round bottom flask. To this stirring solution 1.00 mL (3.36 mmol) of Ti(O-*i*-Pr)$_4$ was slowly added, causing the immediate formation of a yellow color. The flask was fitted with a reflux condenser and removed from the glovebox and the solution refluxed for 12 h. After cooling to room temperature, the volume of the solution was reduced *in vacuo* until a large amount of solid had formed. The mixture was heated in a beaker of sand using a hot plate, until the solid dissolved. The solution was allowed to slowly cool to room temperature and was left undisturbed for 12 h, resulting in the formation of large yellow crystals. The flask was returned to the glovebox, and the solvent was removed using a disposable pipet. The solid was washed with cold hexane and briefly dried *in vacuo*, yielding 2.30 g (89.8%) of product as a toluene solvate. The crude product was recrystallized from toluene by adding a minimal amount of solvent and heating the solution to cause dissolution. Very large yellow crystals were formed when the solution was slowly cooled to room temperature. Anal. Calcd for Ti$_2$O$_{10}$F$_{30}$C$_{55}$H$_{38}$: C, 43.33; H, 2.52. Found: C, 43.13; H, 2.51.

^{1}H NMR (benzene-d_6): δ 4.48 (5H, septet, $^3J_{HH}$ = 6.0 Hz, C*H*Me$_2$); δ 3.66 (3H, broad, O*H*); δ 1.07 (26H, doublet, $^3J_{HH}$ = 6.1 Hz, CH*Me*$_2$).

^{19}F NMR (benzene-d_6): δ −84.97 (2F, broad doublet, J = 7.1 Hz); δ −90.52 (2F, triplet, J = 20 Hz); δ −94.14 (1F, broad triplet, J = 22 Hz, para).

IR (cm^{-1}): 3268 (br, m), 1652 (w), 1627 (w), 1517 (vs), 1471 (vs), 1367 (ms), 1338 (ms), 1313 (ms), 1246 (mw), 1172 (s), 1127 (vs), 1112 (vs), 1022 (vs), 995 (vs), 939 (s), 860 (ms), 821 (ms), 785 (vw), 734 (m), 695 (m), 664 (ms), 635 (s), 605 (s), 599 (m), 544 (ms), 520 (ms).

Ti(O-2,6-F$_2$C$_6$H$_3$)$_3$(O-*i*-Pr) (3). In a Schlenk flask fitted with a reflux condenser, 2.04 g (15.7 mmol) of HO-2,6-F$_2$C$_6$H$_3$, 1.00 mL (3.36 mmol) of Ti(O-*i*-Pr)$_4$, and 20 mL of toluene were refluxed for 12 h. The volume was reduced *in vacuo* to *ca.* 5 mL, producing an orange solid. The mixture was again heated to cause dissolution of the solid and slowly cooled to room temperature causing the formation of orange crystals. The solvent was removed from the solid by decanting using a cannula. The solid was dried *in vacuo*, yielding 1.22 g (73.5%) of

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[35] (a) Crespo, M.; Martinez, M.; Sales, J. *J. Chem. Soc., Chem. Commun.* **1992**, 822. (b) Lucht, B. L.; Poss, M. J.; King, M. A.; Richmond, T. G. *J. Chem. Soc., Chem. Commun.* **1991**, 400. (c) Richmond, T. G.; Osterberg, C. E.; Arif, A. M. *J. Am. Chem. Soc.* **1987**, *109*, 109. (d) Anderson, C. M.; Puddephatt, R. J.; Ferguson, G.; Lough, A. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1297. (e) Anderson, C. M.; Crespo, M.; Ferguson, G.; Lough, A. J.; Puddephatt, R. J. *Organometallics* **1992**, *11*, 1177. (f) Burns, C. J.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1989**, 136.

[36] The chemical shift of CF$_3$CO$_2$H relative to CFCl$_3$ (0 ppm) is reported to be −76.53 ppm. See: Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972.

product. Anal. Calcd for $TiO_4F_6C_{21}H_{16}$: C, 51.03; H, 3.27. Found: C, 50.93; H, 3.16.

^{1}H NMR (benzene-d_6): δ 6.0–6.6 (9H, multiplets, meta and para); δ 5.19 (1H, septet, $^3J_{HH}$ = 6.1 Hz, C*H*Me$_2$); δ 1.43 (6H, doublet, $^3J_{HH}$ = 6.1 Hz, CH*Me*$_2$).

^{19}F NMR (benzene-d_6): δ −53.4 (singlet).

IR (cm^{-1}): 1892 (mw), 1837 (w), 1816 (w), 1766 (w), 1741 (w), 1721 (w), 1647 (mw), 1613 (m), 1589 (ms), 1559 (m), 1505 (vs), 1477 (vs), 1369 (ms), 1322 (s), 1306 (vs), 1241 (vs), 1218 (s), 1171 (m), 1151 (m), 1133 (ms), 1105 (s), 1059 (s), 1017 (vs), 995 (vs), 955 (m), 947 (m), 910 (vs), 864 (s), 848 (s), 770 (s), 738 (s), 724 (s), 711 (s), 635 (m), 610 (s), 599 (ms), 506 (s), 490 (s).

Ti(O-2,4-F$_2$C$_6$H$_3$)$_4$(HO-*i*-Pr) (4). A mixture of 1.84 g (14.2 mmol) of 2,4-difluorophenol, 1.00 mL of Ti(O-*i*-Pr)$_4$ (3.36 mmol), and 20 mL of toluene was refluxed for 12 h. After the volume of the solution was reduced *in vacuo*, the solution was cooled to −35 °C, producing orange crystals. The solvent was decanted and the solid was dried *in vacuo* for 2 h, producing 1.72 g (81.9%) of product. Anal. Calcd for $TiO_5F_8C_{27}H_{20}$: C, 51.94; H, 3.24. Found: C, 51.66; H, 3.58.

^{1}H NMR (benzene-d_6): δ 6.2–7.25 (9H, multiplets); δ 5.06 (1H, broad singlet, O*H*); δ 5.19 (1H, septet, $^3J_{HH}$ = 6.3 Hz, C*H*Me$_2$); δ 1.11 (6H, doublet, $^3J_{HH}$ = 6.3 Hz, CH*Me*$_2$).

^{19}F NMR (benzene-d_6): δ −52.21 (1F, broad singlet); δ −42.77 (1F, singlet).

IR (cm^{-1}): 3435 (broad, m), 3084 (mw), 1698 (w), 1596 (m), 1561 (mw), 1504 (vs), 1435 (s), 1396 (m), 1379 (m), 1318 (s), 1302 (s), 1283 (ms), 1255 (vs), 1203 (vs), 1140 (vs), 1100 (s), 1011 (ms), 965 (ms), 927 (m), 882 (vs), 842 (vs), 813 (vs), 728 (ms), 698 (w), 605 (vs), 598 (w), 519 (s).

Ti(O-4-FC$_6$H$_4$)$_4$(HO-*i*-Pr) (5). A mixture of 1.60 g (14.3 mmol) of 4-fluorophenol, 1.00 mL of Ti(O-*i*-Pr)$_4$ (3.36 mmol) and 20 mL of toluene was refluxed for 12 h. The volume of the solution was reduced *in vacuo* producing an orange crystalline solid. The remaining solvent was removed using a pipet. The crude product appeared to incorporate a solvent molecule in the crystal lattice. The crystals become opaque and ultimately become powder over a period of several hours in the drybox or when exposed to vacuum. The crude product was washed with hexane and dried *in vacuo* (10^{-3} Torr) for 12 h producing 1.16 g (62.4%) of a yellow powder.

^{1}H NMR (benzene-d_6): δ 6.72, 6.65 (16H, singlets, ortho and meta); δ 4.10 (1H, septet, $^3J_{HH}$ = 6.1 Hz, C*H*Me$_2$); δ 0.93 (6H, doublet, $^3J_{HH}$ = 6.1 Hz, CH*Me*$_2$).

^{19}F NMR (benzene-d_6): δ −45.7 (singlet).

IR (cm^{-1}): 3279 (br, ms), 3106 (m), 3079 (m), 3052 (m), 2066 (w), 2006 (w), 1863 (mw), 1752 (w), 1731 (w), 1631 (mw), 1596 (mw), 1499 (vs), 1412 (ms), 1339 (ms), 1268 (s), 1201 (s), 1166 (ms), 1146 (ms), 1119 (s), 1088 (s), 1018 (ms), 962 (ms), 938 (ms), 900 (s), 842 (s), 802 (s), 767 (s), 710 (mw), 640 (ms), 603 (s), 597 (w), 590 (w), 492 (vs).

Ti(OC$_6$H$_5$)$_4$(HO-*i*-Pr) (6). With stirring, 1.00 mL (3.36 mmol) of Ti(O-*i*-Pr)$_4$ was slowly added to a toluene (20 mL) solution containing 1.32 g (14.0 mmol) of phenol, causing the immediate formation of an orange solution. The solution was refluxed for 12 h. The volume of the solution was then reduced until a large amount of an orange solid had formed. The solution was decanted and the solid washed with hexane and dried *in vacuo*, producing 1.20 g (74.5%) of crude product, which was recrystallized from toluene. Anal. Calcd for $TiO_5C_{27}H_{28}$: C, 67.50; H, 5.89. Found: C, 67.68; H, 6.02.

^{1}H NMR (benzene-d_6): δ 7.2–6.7 (20H, ortho, meta, and para); δ 6.37 (1H, br s, O*H*); δ 4.63 (septet, 1 H,$^3J_{HH}$ = 6.1 Hz, C*H*Me$_2$); δ 1.37 (6H, doublet, $^3J_{HH}$ = 6.1 Hz, CH*Me*$_2$)

IR (cm^{-1}): 3190 (br, mw), 3065 (mw), 1939 (mw), 1852 (mw), 1784 (mw), 1721(mw), 1586 (s), 1411 (m), 1336 (m), 1276 (s), 1250 (vs), 1218(vs), 1162 (s), 1117 (ms), 1068 (m), 1022 (m), 1000 (m), 940 (m), 896 (s), 854 (ms), 839 (ms), 820 (ms), 755 (s), 690 (ms), 661 (ms), 611 (ms), 559 (ms), 529 (ms), 487 (ms).

Ti[OCH(CF$_3$)$_2$]$_2$(OEt)$_2$(HOEt) (7). A mixture of 2.00 mL of Ti(OEt)$_4$ (9.50 mmol), 20 mL of toluene, and a large excess of HOCH(CF$_3$)$_3$ (*ca.* 20 mL, 189 mmol) was refluxed for 12 h in a Schlenk flask. The solvent was removed *in vacuo*, yielding 2.80 g (56.9%) of the colorless crude product. Recrystallization from a concentrated toluene solution at −40 °C produced large crystals. Anal. Calcd for $TiO_5F_{12}C_{12}H_{18}$: C, 27.82; H, 3.51. Found: C, 27.41; H, 3.53.

^{1}H NMR (60 °C, toluene-d_8): δ 4.99 (2H, broad, C*H*(CF$_3$)$_2$); δ 4.52 (6H, quartet, $^3J_{HH}$ = 7.1 Hz, C*H*$_2$CH$_3$); δ 1.41 (9H, triplet, $^3J_{HH}$ = 7.0 Hz, CH$_2$C*H*$_3$).

^{19}F NMR (60 °C, toluene-d_8): δ −0.42 (doublet, $^3J_{HF}$ = 4.9 Hz, CH(C*F*$_3$)$_2$.

IR (cm^{-1}): 3290 (br, m), 1406 (ms), 1365 (vs), 1286 (vs), 1260 (vs), 1216 (vs), 1189 (vs), 1151 (vs), 1105 (vs), 1076 (s), 1034 (s), 937 (ms), 888 (s), 856 (vs), 815 (w), 751 (s), 687 (s), 599 (s), 583 (ms), 514 (s).

Ti(OC$_6$F$_5$)$_3$(OEt)(HOEt) (8). In a Schlenk flask a mixture of Ti(OEt)$_4$ (1.00 mL, 4.75 mmol) and 3.68 g (20.0 mmol) of HOC$_6$F$_5$ in 20 mL of toluene was refluxed for 12 h. The solvent was removed *in vacuo*, producing an orange oil, which was triturated with hexane producing a yellow-orange powder. The powder was dried *in vacuo* for 12 h to remove any excess phenol. The yield of this crude product was 2.68 g (82.0%). Recrystallization from toluene produced an oily solid, which was washed with hexane to produce a yellow powder. The final product appeared to be identical to the crude product based on NMR and IR spectroscopies. Anal. Calcd for $TiO_5F_{15}C_{22}H_{11}$: C, 38.40; H, 1.61. Found: C, 38.40; H, 1.60.

^{1}H NMR (benzene-d_6): δ 4.65 (broad, O*H*); δ 4.35 (2H, quartet, $^3J_{HH}$ = 6.8 Hz, C*H*$_2$CH$_3$); δ 1.12 (3H, triplet, $^3J_{HH}$ = 6.8 Hz, CH$_2$C*H*$_3$).

^{19}F NMR (benzene-d_6): δ −85.92 (2F, broad, ortho); δ −89.42 (2F, triplet, J = 19.5 Hz); δ −91.91 (1F, broad, para).

IR (cm^{-1}): 3028 (br, ms), 2728 (mw), 2669 (mw), 2384 (w), 1800 (w), 1771 (w), 1750 (w), 1718 (w), 1698 (w), 1682 (w), 1652 (m), 1631 (m), 1604 (m), 1514 (s), 1498 (s), 1465 (vs), 1376 (s), 1316 (s), 1266 (m), 1250 (m), 1180 (ms), 1169 (ms), 1152 (ms), 1106 (ms), 1074 (ms), 1029 (s), 995 (s), 980 (s), 943 (ms), 874 (m), 815 (mw), 785 (mw), 730 (s), 694 (s), 675 (ms), 635 (ms), 609 (ms), 600 (ms), 582 (ms), 543 (ms), 526 (ms), 496 (ms).

Ti(O-2,6-F$_2$C$_6$H$_3$)$_3$(OEt)(HOEt) (9). In a Schlenk flask, 1.00 mL (4.75 mmol) of Ti(OEt)$_4$, 2.60 g (20 mmol), and 20 mL of toluene were refluxed for 12 h. The solvent was removed *in vacuo*. The resulting orange powder was washed with hexane and dried *in vacuo* for 2 h, producing 1.50 g (60.0%) of the product.

^{1}H NMR (toluene-d_8): δ 6.0–6.6 (9H, multiplets, meta and para); δ 4.89 (4H, quartet, $^3J_{HH}$ = 6.9 Hz, C*H*$_2$CH$_3$); δ 4.31 (1H, singlet, O*H*); δ 1.46 (6H, triplet, $^3J_{HH}$ = 7.0 Hz, CH$_2$C*H*$_3$).

^{19}F NMR (benzene-d_6): δ −53.83 (broad).

IR (cm^{-1}): 3510 (br, m), 1588 (m), 1564 (mw), 1499 (vs), 1476 (s), 1352 (mw), 1307 (s), 1242 (s), 1150 (w), 1118 (m), 1087 (mw), 1062 (ms), 1034 (m), 1006 (s), 940 (w), 898 (s), 847 (ms), 770 (ms), 738 (ms), 726 (ms), 710 (ms), 605 (ms), 597 (ms).

Ti(O-2,4-F$_2$C$_6$H$_3$)$_4$(HOEt) (10). A mixture of 1.00 mL (4.75 mmol) of Ti(OEt)$_4$, 3.16 g (24.3 mmol) of 2,4-difluorophenol, and 20 mL of toluene was refluxed for 12 h, after which the solvent was removed *in vacuo*. The product was washed with hexane and filtered, yielding 1.49 g (51.4%) of an orange powder that was recrystallized from toluene to provide orange-red plates.

^{1}H NMR (benzene-d_6): δ 6.95–6.17 (12H, multiplets); δ 5.88 (broad, O*H*); δ 4.32 (2H, quartet, $^3J_{HH}$ = 6.8 Hz, C*H*$_2$CH$_3$), δ 1.20 (3H, triplet, $^3J_{HH}$ = 6.8 Hz, CH$_2$C*H*$_3$).

^{19}F NMR (benzene-d_6): δ −52.45 (1F, broad singlet); δ −42.40 (1F, singlet).

IR (cm^{-1}): 3318 (br, m), 3108 (m), 3084 (m), 1862 (w), 1663 (w), 1602 (s), 1559 (w), 1502 (vs), 1453 (s), 1435 (s), 1407 (ms), 1378 (m), 1316 (vs), 1279 (ms), 1252 (vs), 1204 (vs), 1140 (vs), 1097 (s), 1081 (ms), 1035 (ms), 965 (s), 878 (vs), 848 (vs), 810 (vs), 728 (s), 713 (m), 696 (mw), 599 (vs), 515 (s), 492 (s).

Ti(O-4-FC$_6$H$_4$)$_4$(HOEt) (11). A mixture of 1.00 mL (4.75 mmol) of Ti(OEt)$_4$, 2.27 g (20.3 mmol) of 4-fluorophenol, and 20 mL of toluene was refluxed for 12 h, after which the solvent was removed *in vacuo*. The resulting crude product was washed with hexane and recrystallized from toluene, providing 1.89 g (73.8%) of an orange-red crystalline product.

^{1}H NMR (benzene-d_6): δ 6.73, 6.66 (16H, singlets, ortho and meta); δ 6.23 (1H, broad, O*H*); δ 3.77 (2H, broad quartet, C*H*$_2$CH$_3$), δ 0.94 (3H, broad triplet, CH$_2$C*H*$_3$).

^{19}F NMR (benzene-d_6): δ −45.5 (singlet).

IR (cm^{-1}): 3192 (br, m), 3050 (m), 1864 (m), 1732 (w), 1635 (mw), 1596 (mw), 1496 (vs), 1454 (ms), 1417 (ms), 1354 (w), 1261 (s), 1219 (s), 1200 (vs), 1144 (ms), 1111 (m), 1087 (ms), 1039 (ms), 1013 (w), 892 (s), 832 (s), 802 (s), 785 (s), 769 (s), 708 (mw), 671 (w), 642 (m), 593 (ms), 583 (w), 545 (m), 490 (s).

$Ti(OC_6H_5)_4(HOEt)$ (12). A mixture of 1.00 mL (4.75 mmol) of $Ti(OEt)_4$, 1.88 g (20.0 mmol) of phenol, and 20 mL of toluene was refluxed for 12 h. The volume of the solution was reduced *in vacuo* until a large amount of solid had formed. The solid was redissolved by heating and allowed to cool to room temperature. The solvent was decanted and the solid was dried *in vacuo*, yielding 1.81 g (81.5%) of the orange powder.

^{1}H NMR (benzene-d_6): δ 7.1–6.6 (20H, ortho, meta, and para); δ 5.94 (1H, br, O*H*); δ 4.15 (broad, 2H, CH_2CH$_3$); δ 1.10 (3H, CH$_2$CH_3)

IR (cm^{-1}): 3058 (br, mw), 1935 (w), 1850 (w), 1782 (w), 1722 (w), 1657 (w), 1587 (ms), 1482 (vs), 1342 (w), 1276 (ms), 1252 (s), 1215 (ms), 1163 (m), 1115 (w), 1088 (w), 1069 (mw), 1042 (mw), 1023 (m), 999 (mw), 906 (s), 854 (m), 839 (m), 823 (m), 756 (s), 729 (m), 689 (ms), 662 (ms), 651 (ms), 626 (m), 609 (m), 605 (m), 582 (m), 558 (m), 491 (ms).

$Ti(O\text{-}2,6\text{-}F_2C_6H_3)_2(O\text{-}i\text{-}Pr)_2$ (13). The procedure was similar to that used to prepare **3** except that only 2 equiv of $HO\text{-}2,6\text{-}F_2C_6H_3$ were used. The yield was 36% based on Ti(O-*i*-Pr)$_4$. Anal. Calcd for $TiO_4F_4C_{18}H_{20}$: C, 50.91; H, 4.76. Found: C, 51.09; H, 4.60.

^{1}H NMR (benzene-d_6): δ 6.5 and 6.2 (6H, multiplets, meta and para); δ 4.8 (2H, septet, $^3J_{HH}$ = 6.1 Hz, C*H*Me$_2$); δ 1.3 (12H, doublet, $^3J_{HH}$ = 6.1 Hz, CH*Me*$_2$).

$Ti[OCH(CF_3)_2]_4$ (14). *Caution*! Both $TiCl_4$ and $Ti[OCH(CF_3)_2]_4$ fume on exposure to moist air. The compound was prepared using a variation of the procedure published by Mazdiyasni and coworkers.[11] In the drybox, 2.28 g (95.0 mmol) of NaH were placed in a solids addition tube, after which it was removed from the drybox. Toluene and *ca.* 25 mL of $HOCH(CF_3)_2$ were mixed in a Schlenk flask containing a magnetic stir bar. The NaH was slowly added to this ice-cooled solution, causing effervescence of H_2. After all the NaH was added, the flask was fitted with a reflux condenser and refluxed for 6 h. The solution was cooled to ice temperature, and the reflux condenser was replaced by a septum cap, through which 2.60 mL (23.8 mmol) of $TiCl_4$ was slowly added using a syringe. The septum cap was replaced by the reflux condenser and the resulting yellow suspension was stirred and refluxed for 12 h. After cooling the colorless suspension, the volatile liquids were removed *in vacuo* from the solid product. The $Ti[OCH(CF_3)_2]_4$ was recovered by distillation under dynamic vacuum into a liquid nitrogen cooled trap. The crude product was purified by vacuum (static) distillation, collecting the fraction boiling between 39 and 43 °C, yielding 15.4 g (90.6%) of a clear liquid.

^{1}H NMR (benzene-d_6): δ 4.18 (septet, $^3J_{HF}$ = 5.4 Hz, C*H*(CF$_3$)$_2$).

^{19}F NMR (benzene-d_6): δ −8.89 (doublet, $^3J_{HF}$ = 5.6 Hz, CH(C*F*$_3$)$_2$).

$Ti[OCH(CF_3)_2]_4(N{\equiv}CMe)_2$ (15). $Ti[OCH(CF_3)_2]_4$ (*ca.* 1 mL) was dissolved in 20 mL of acetonitrile. After several minutes the solvent was removed *in vacuo* producing a colorless solid. The solid was sealed in an ampule (10^{-3} Torr) and sublimed at 45 °C, producing colorless cubes. Anal. Calcd for $TiO_4F_{24}C_{16}H_{10}N_2$: C, 24.06; H, 1.25; N, 3.50. Found: C, 23.04; H, 1.13; N, 3.45.

^{1}H NMR (benzene-d_6): δ 2.43 (3H, septet, $^3J_{HF}$ = 5 Hz, C*H*(CF$_3$)$_2$); δ 2.23 (1H, septet, $^3J_{HF}$ = 5 Hz, C*H*(CF$_3$)$_2$); δ 0.86 (6H, singlet, N≡C*Me*).

^{19}F NMR (benzene-d_6): δ 0.69 (1F, broad, CH(C*F*$_3$)$_2$); δ 0.03 (3F, broad doublet, $^3J_{HF}$ = 4.6, CH(C*F*$_3$)$_2$).

IR (cm^{-1}): 2322 (m), 2295 (ms), 1288 (vs), 1259 (vs), 1189 (vs), 1145 (vs), 1104 (vs), 1038 (mw), 939 (mw), 892 (s), 853 (vs), 756 (vs), 702 (ms), 687 (s), 601 (w), 594 (ms).

$Ti[OCH(CF_3)_2]_4(THF)_2$ (16). THF (4 mL) was added to 20 mL of a hexane solution containing **14** (*ca.* 1 mL). After several minutes the solvent was removed *in vacuo* producing a colorless powder, which was recrystallized from hexane.

^{1}H NMR (toluene-d_8): δ 5.25 (4H, septet, $^3J_{HF}$ = 5.3 Hz, C*H*(CF$_3$)$_2$); δ 3.39 (8H, multiplet, α-CH$_2$); δ 1.57 (8H, multiplet, *β*-C*H*$_2$).

^{19}F NMR (toluene-d_8): δ −0.38 (doublet, $^3J_{HF}$ = 5.3 Hz, CH(C*F*$_3$)$_2$).

IR (cm^{-1}): 1293 (vs), 1260 (vs), 1220 (vs), 1195 (vs), 1150 (vs), 1110 (vs), 1044 (ms), 1015 (s), 966 (m), 918 (ms), 895 (s), 850 (s), 768 (s), 753 (s), 720 (ms), 687 (s), 601 (mw), 594 (ms), 592 (ms).

Crystallographic Studies. Crystal data for **2**, **3**, **7**, and **15** are given in Table 1. Suitable crystals were sealed in glass capillary tubes under an inert atmosphere and mounted on the goniometer of an Enraf-Nonius CAD-4 diffractometer. Data were collected and reduced using standard procedures.[37] Structures were solved by direct methods using SIR (**2**),[38] MULTAN (**3**),[39] or SHELX-86 (**7** and **16**).[40] Difference maps phased on the results from these programs readily revealed the positions of the non-hydrogen atoms. Disorder was observed and accounted for in one isopropyl group (3:2 ratio) and the solvent molecule (disordered over an inversion center) of **2**. After absorption correction,[41] in all cases the Ti atom was refined anisotropically. Additional atoms treated in this manner were the oxygen and fluorine atoms of **2**, the fluorine atoms of **7**, and all other non-hydrogen atoms of **15**. In all cases the fluorine atoms appeared to have large thermal motion that did not appear to be a result of disorder. Hydrogen atoms were included in the models in calculated positions with isotropic thermal parameters such that $B(H) = 1.3B_{eq}$ of the attached non-hydrogen atom. The chirality of **15** was confirmed by attempting to fit the data to the other enantiomeric form, which resulted in a much higher *R* factor.

After the final cycles of least squares refinement, the maximum shift of a parameter was less than 0.02 (**7**) or 0.01 (**2**, **3**, **15**) of its estimated standard deviation and the final difference maps showed no feature higher than 0.72 e/Å^3 (**2**, close to the solvent molecule), 0.42 e/Å^3 (**3**, near F(30)), 0.42 e/Å^3 (**6**, near C(7)) and 0.57 e/Å^3 (**15**, near the fluorines of C(11)). Scattering factors were taken from Cromer and Weber,[42] and anomalous dispersion effects were included in F_c using the values of Cromer.[43] Plots of $(|F_o| - |F_c|)_2$ vs F_o, sin θ, or data collection order showed no unusual trends. All computations, except where stated, were carried out using the MolEN suite of computer programs.[44]

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Supplementary Material Available: ORTEP drawings with complete atom numbering schemes, tables of anisotropic thermal parameters, and complete listings of bond distances and angles for **2**, **3**, **7**, and **15** (47 pages). Ordering information is given on any current masthead page. This material has also been deposited with the Cambridge Crystallographic Data Centre.

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(37) Mason, M. R.; Smith J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 4971.

(38) Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spangna, R.; Viterbo, D. *J. Appl. Crystallogr.* **1989**, *22*, 389.

(39) Main, P. Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; DeClerq, J. P.; Woolfson, M. M. *MULTAN80, A System of Computer Programs for the Automatic Solution of Crystal Structure from X-ray Diffraction Data*; University of York: York, England, 1980.

(40) Sheldrick, G. M. in *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, England, 1985; p 175.

(41) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 159.

(42) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974, Vol. IV, Table 2.

(43) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(44) *MolEN, An Interactive Structure Solution Program*; Enraf-Nonius: Delft, The Netherlands, 1990.