3188 *Inorg. Chem.* **1996,** *35,* 3188−3193

Synthesis and Reaction Chemistry of the Disodium Alkoxide of 2,6-Bis(trifluoromethyl)-2,6-dihydroxy-3,3,4,4,5,5-hexafluorooxane

John D. O. Anderson, William T. Pennington, and Darryl D. DesMarteau*

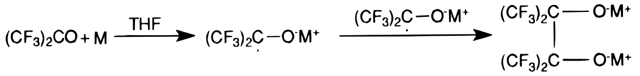
H. L. Hunter Chemistry Laboratory, Clemson University, P.O. Box 341905,
Clemson, South Carolina 29634-1905

Received July 7, 1995[⊗]

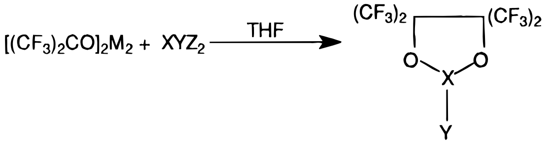
The disodium alkoxide of 2,6-bis(trifluoromethyl)-2,6-dihydroxy-3,3,4,4,5,5-hexafluorooxane, $C_7F_{12}O_3Na_2$, **1**, was prepared by reaction of the corresponding diol with MeONa in MeOH. This cyclic alkoxide readily mimics the reaction chemistry of the lithium and sodium alkoxides of perfluoropinacol. The reaction of the alkoxide **1** with covalent dichlorides and metallocene dichlorides yields a series of novel bicyclic ring systems. The crystal structure of the trioxasilane, **3**, formed from $(CH_3)_2SiCl_2$ was determined to provide structural information about these ring systems. Crystal data: $C_9H_6O_3F_{12}Si$, fw = 418.21 u, orthorhombic space group, *Pnma* (No. 62), $a = 15.822(3)$ Å, $b = 12.163(3)$ Å, $c = 7.373(2)$ Å, $V = 1418.9(4)$ Å^3, and $D_{calc} = 1.96$ g cm^{-3} for $Z = 4$ (molecule possesses mirror symmetry). Least-squares refinement on 1075 observed reflections ($I > 3\sigma(I)$) converged with $R = 0.0357$ and $R_w = 0.0478$.

Introduction

The reductive coupling of hexafluoroacetone (HFA) with alkali metals in a donor solvent to yield perfluoropinacolate was reported in the late 1960's by Frye[1] and Willis.[2] Due to the high electrophilicity of HFA, the first step in its reaction with sodium is presumably an electron transfer to give bis(trifluoromethyl)ketyl, which then couples with another ketyl molecule.

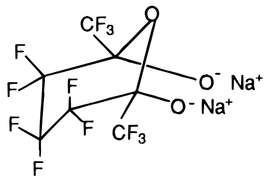


In support of this mechanism Janzen and Gerlock[3] reported that bis(trifluoromethyl)ketyl may exist as a stable radical in acetonitrile solution. This chemistry provided a convenient route to the dialkoxides of perfluoropinacol and led to the preparation of numerous cyclic derivatives by reaction of the dialkoxide of perfluoropinacol with covalent dihalides.[4−6]



where M = Li, Na; X = B, C, Si, Ge, Sn, P, S; Y = functional group(s); Z = Cl, F.

The recent report of a novel diol derived from $[CF_3C(O)CF_2]_2CF_2$[7] provided a route to the new alkoxide **1**.



1

Table 1. Crystallographic Data for **3**

formula	$C_9H_6O_3F_{12}Si$
formula weight	418.21
crystal dimensions (mm)	0.23 × 0.24 × 0.31
crystal system	orthorhombic
space group	*Pnma* (No. 62)
unit cell dimensions	
a (Å)	15.822(3)
b (Å)	12.163(3)
c (Å)	7.373(2)
V (Å^3)	1418.9(4)
Z	4
D_{calc} (g/cm^3)	1.96
reflections collected	1322
R^a	0.0357
$R_w{}^b$	0.0428
$(\Delta/\sigma)_{max}$	0.01
reflections observed ($I > 3\sigma(I)$)	1075
$\Delta\rho_{max}/\Delta\rho_{min}$ (e$^-$/Å^3)	0.50/−0.22

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.

A study of the reactions of **1** with several Group 4 and 13−15 dihalides was undertaken for comparison with perfluoropinacol. These reactions gave excellent yields of many new bicyclic heterocycles, but some reactions failed due to the instability of the products or lack of reaction due to the low nucleophilicity of **1**.

Experimental Section

General Methods. Compounds were manipulated and characterized as described previously.[7] A typical reaction vessel for preparation of **1** and its reactions was a 100 mL reactor as previously described.[7]

X-ray Crystallographic Analysis. Structure analysis of **3** was carried out at −70 ± 1 °C using procedures described previously.[7] Relevant crystallographic data are given in Table 1.

Reagents. Acetonitrile was dried over CaH_2 and distilled from P_2O_5 (≤5 g/L), sulfolane was distilled from CaH_2 under vacuum, and reagent grade tetrahydrofuran was distilled from sodium diphenylketyl. Anhydous methanol (Baxter) was stored over 3 Å molecular sieves while ethyl ether was dried over NaH. Titanocene dichloride, zirconocene dichloride, hafnocene dichloride, $(CH_3)_2SiCl_2$, $SiCl_4$, and CH_3OPCl_2 were obtained from Aldrich. Tetrafluoroethylene was purchased from PCR Inc. and used without further purification. 1,2-Dichlorotetrafluorocyclobutene-1 was obtained by standard methods from 1,1,2,2-tetrachlorotetrafluorocyclobutane (PCR Inc.).

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1996.

(1) Frye, C. L.; Salinger, R. M.; Patin, T. J. *J. Am. Chem. Soc.* **1966**, *88*, 2343−2344.

(2) Janzen, A. F.; Rodesiler, P. F.; Willis, C. J. *Chem. Commun.* **1966**, 672.

(3) Janzen, E. G.; Gerlock, J. L. *J. Phys. Chem.* **1967**, *71*, 4577.

(4) Allan, M.; Janzen, A. F.; Willis, C. J. *Chem. Commun.* **1968**, 55.

(5) Allan, M.; Janzen, A. F.; Willis, C. J. *Can. J. Chem.* **1968**, *46*, 3671.

(6) Conroy, A. P.; Dresdner, R. D. *Inorg. Chem.* **1970**, *9*, 2739.

(7) Anderson, J. D. O.; Pennington, W. T.; DesMarteau, D. D. *Inorg. Chem.* **1993**, *32*, 5079.

S0020-1669(95)00843-3 CCC: $12.00

Preparation of the Disodium Alkoxide

$$CF_3(^+Na^-O)\overline{C(CF_2)_3CO}(O^-Na^+)CF_3$$

1. The cyclic diol of 2,6-perfluoroheptadione (10.1 mmol) was prepared in a reactor in the usual manner.[7] Sodium methoxide (1.08 g, 20.0 mmol) was dissolved in dry methanol (15 mL) and injected into the reactor, cooled at 0 °C, through a septum. The flask containing the NaOMe was washed with two 5 mL portions of dry methanol which were added to the reactor containing the diol. The reactor was stirred at 0 °C for 2 h and then for an additional 2 h at 25 °C.

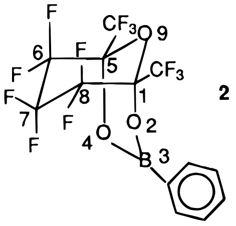
The contents of the reactor were transferred to a 100 mL flask, along with two 5 mL portions of dry methanol used to rinse the reactor. The methanol was removed under vacuum, and the flask was then heated to 70 °C and held under dynamic vacuum for 4 days to remove any residual methanol. Compound **1** (3.75 g, 9.24 mmol, 91.6%) was obtained as a white solid.

1 was characterized as follows: IR (KBr) 1691 (w), 1612 (w), 1361 (sh, m), 1303 (vs), 1237 (vs), 1163 (vs), 1000 (vs), 962 (s), 918 (vs), 830 (m), 739 (m), 689 (m), 647 (w), 626 (w), 576 (m), 530 (w), 461 (vw) cm^{-1}; NMR

$$CF_3^{C}(^+Na^-O)\overline{CCF^AF^BCF^CF^DCF^AF^BCO}(O^-Na^+)CF_3^{C}$$

(acetone-d_6, 24 °C) δ ^{19}F C −81.5 (6F, m), A −125.8, B −128.7 (4F, AB pattern), C −116.7, D −139.2 (2F, AB pattern) ppm; $J_{AB} = 256.1$, $J_{CD} = 274.8$ Hz.

Reaction of 1 with $C_6H_5BCl_2$. Compound **1** (0.33 g, 0.81 mmol) was placed in a 50 mL reactor, and the reactor was evacuated. It was cooled to 0 °C, and pentane (0.5 mL) and phenylboron dichloride (0.10 mL, 0.76 mmol) were added to the flask by syringe. The reaction mixture was stirred for 3.5 h at 0 °C. The volatiles were removed under vacuum through traps at −49 and −196 °C. The −49 °C trap contained a clear colorless liquid with a low vapor pressure (<1 Torr, 22 °C) (0.30 g, 88% yield) 1,5-bis(trifluoromethyl)-6,6,7,7,8,8-hexafluoro-3-phenyl-2,4,9-trioxa-3-borabicyclo[3.3.1]nonane (**2**).

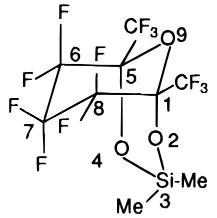


2

2 was characterized as follows: IR (neat, KCl) 3045 (s), 2809 (vw), 2702 (vw), 2556 (w), 2447 (w), 2154 (vw), 2107 (vw), 1956 (w), 1896 (w), 1809 (m), 1679 (w), 1594 (s), 1488 (s), 1430 (s), 1335 (vs), 1294 (vs), 1237 (vs), 1186 (vs), 1133 (s), 1101 (s), 1057 (s), 1014 (s), 997 (s), 984 (s), 890 (vs), 844 (s), 753 (s), 735 (s), 688 (vs), 634 (s), 602 (s), 540 (s) cm^{-1}; NMR (C_6D_6, 24 °C) δ ^1H 7.65−7.62 (2H, m), 7.14−7.10 (1H, m), 7.00−6.94 (2H, m), δ ^{19}F CF_3 −79.7 (6F, m), F-6, F-8 −124.4, −130.9 (4F, AB pattern), F-7 −113.3, −137.4 (2F, AB pattern); $^2J_{F6,F8} = 269.5$, $^2J_{F7} = 283.4$ Hz; MS [EI] *m/e* 448 (56.7, M^+), 131 (32.9, $CF_3CCF_2^+$), 109 (20.7, CF_3COC^+), 100 (61.0, $CF_2CF_2^+$), 93 (16.5, CF_3CC^+), 81 (11.6, CF_3C^+), 78 (17.7, CF_2CO^+), 77 (9.8, $C_6H_5^+$), 69 (100.0, CF_3^+), 50 (29.3, CF_2^+); [CI] *m/z* 449 (7.5, MH^+), 248 (14.2, M-$C_4F_8^+$), 229 (100.0, M-$C_3F_7^+$), 209 (15.4, $OC(CF_3)CF_2CF_2C^+$), 148 (21.7, $C_6H_5BO_2CO^+$), 131 (7.9, $C_3F_5^+$), 100 (9.4, $C_2F_4^+$).

Reaction of 1 with $SiCl_4$. A 25 mL 3 necked flask with septum arm was loaded with the alkoxide $C_7F_{12}O_3Na_2$ (0.35 g, 0.86 mmol). The flask was evacuated, and pentane (10 mL) followed by $SiCl_4$ (0.05 mL, 0.44 mmol) was added to the flask. The flask was initially kept at 0 °C with stirring and allowed to warm slowly to 25 °C over a 12 h period. The volatile components were removed under vacuum through traps at −50 and −196 °C. The −196 °C trap contained pentane while the −50 °C trap contained no material. The remaining white solid in the flask was extracted with acetone (10 mL) to give 0.31 g of a white solid extract after removal of the acetone. The solid appeared to be polymeric in nature and was clearly not the desired spiro compound. The material was partially characterized as follows: IR (KBr) 2965 (vw), 1704 (m), 1625 (w), 1426 (w), 1374 (m), 1360 (m), 1325 (m), 1299 (s), 1241 (s), 1171 (m), 1140 (m), 1003 (s), 973 (s), 954 (s), 912 (vs), 830 (s), 804 (s), 736 (s), 689 (s), 647 (m), 628 (m), 575 (s), 537 (m), 461 (w), 398 (w) cm^{-1}; NMR (acetone-d_6) δ ^{19}F CF_3 −81.4 (6F, br), CF_2 −124.2 to −129.7 (4F, v br AB patern), CF_2 −113.4, −117.4, −138.0, −139.4 (2F, br AB pattern).

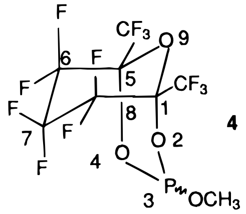
Reaction of 1 with $(CH_3)_2SiCl_2$. A 50 mL reactor containing **1** (0.41 g, 1.01 mmol) was evacuated and cooled to 0 °C. Ether (1 mL) was added via syringe followed by dimethyldichlorosilane (0.12 mL). A white precipitate formed immediately in a slightly exothermic reaction. The mixture was vigorously stirred for 1 h at 0 °C. The volatiles were removed under vacuum through traps at −39 and −196 °C. The −39 °C trap contained a clear colorless solid (0.37 g, 89% yield) of 1,5-bis(trifluoromethyl)-3,3-dimethyl-6,6,7,7,8,8-hexafluoro-2,4,9-trioxa-3-silabicyclo[3.3.1]nonane (**3**).



3

The trioxasilane (**3**) was characterized as follows: mp 39 °C; IR (2 Torr) 2959 (ν_{C-H}, vw), 1367 (w), 1340 (m), 1301 (s), 1247 (vs), 1217 (vs), 1205 (s), 1184 (s), 1127 (s), 1075 (s), 1013 (w), 929 (s), 897 (m), 854 (m), 840 (m), 823 (m), 754 (w), 727 (w), 687 (w), 648 (w), 631 (w) cm^{-1}; NMR ($CDCl_3$, 12.4 °C) δ ^1H 0.59 (3H, s), 0.50 (3H, d), δ ^{19}F CF_3 −81.5 (6F d,d), F-6, F-8 −126.6, −132.2 (4F, AB pattern), F-7 −116.5, −139.3 (2F, AB pattern); $^2J_{F6,F8} = 268.4$, $^2J_{F7} = 279.8$, $^4J_{CF3-F6F8(axial)} = 14.7$, $^4J_{CF3-F6F8(equatorial)} = 7.50$, $^7J_{F7(axial)CH3} = 1.98$ Hz; MS [EI] *m/e* 247 (6.2, $CF_3COCF_2CF_2CF_2^+$), 209 (13.0, $OC(CF_3)CF_2CF_2C^+$), 171 (78.0, $CCF_2CF_2CFCO^+$), 131 (18.2, $C_3F_5^+$), 121 (43.4, $CCF2CFCO^+$), 100 (13.8, $C_2F_4^+$), 97 (12.4, CF_3CO^+), 81 (21.9, CF_3C^+), 77 (100.0, $(CH_3)_2SiF^+$), 69 (21.0, CF_3^+), 59 (11.6, $OSiCH_3^+$), 47 (23.7, SiF^+); [CI] *m/e* 419 (58.2, MH^+), 399 (100.0, $MH-HF^+$), 359 (34.2, $M-OSiCH_3^+$), 337 (32.1, $M-CCF_3^+$), 303 (19.6, $M-(CH_3)_2-O-CF_3^+$), 275 (15.8, $CF_3(O)CCF_2CF_2CF_2CO^+$), 247 (47.3, $CF_3(O)CCF_2CF_2CF_2^+$), 209, (15.8, $OC(CF_3)CF_2CF_2C^+$), 171 (40.2, $CCF_2CF_2CFCO^+$).

Reaction of 1 with CH_3OPCl_2. Into a 25 mL flask fitted with a glass Teflon valve was added 0.33 g, 0.81 mmol, of the disodium alkoxide. The flask was evacuated and cooled to −196 °C. Pentane (0.80 mL) and methyl dichlorophosphite (0.73 mmol) were condensed into the flask by vacuum transfer. The flask was placed in an ice bath at 0 °C and stirred for 2 h. The flask was warmed to 25 °C and stirred for an additional 4 h. The volatile components were removed under dynamic vacuum and through traps at −55 and −196 °C. The −55 °C trap contained 0.25 g of 1,5-bis(trifluoromethyl)-6,6,7,7,8,8-hexafluoro-3-(methyloxy)-2,4,9-trioxa-3-phosphabicyclo[3.3.1]nonane (**4**), a clear viscous liquid (0.59 mmol, 81% yield) as a mixture of exo/endo isomers about P in a (51/49) ratio.

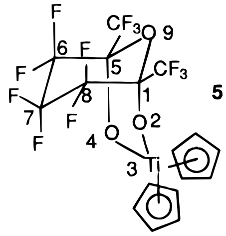


4

The trioxaphosphane **4** was characterized as follows: IR of mixture (2 Torr) 2979 (w), 2857 (vw), 1335 (m), 1303 (s), 1253 (vs), 1213 (s), 1195 (s), 1158 (s), 1115 (s), 1063 (s), 1037 (m), 926 (s), 854 (w), 839 (w), 784 (w), 755 (w), 730 (w), 687 (w), 632 (vw), 602 (vw) cm^{-1}; NMR ($CDCl_3$, 24 °C) δ ^1H 3.84 (3H, d), δ ^{19}F ($CDCl_3$) CF_3 −80.2 (6F, m), F-6, F-8 −126.3, −132.5 (4F, AB pattern), F-7 −116.1, −138.3 (2F, AB pattern), δ ^{31}P 123.0 (d,q) ppm; $^2J_{F6F8} = 269.1$, $^2J_{F7} = 278.5$,

$^3J_{P-H} = 13.27$, $J_{P-F7(axial)} = 16.7$ Hz; minor isomer δ ^{1}H 3.85 (3H, d,d), δ ^{19}F CF_3 −81.0 (6F, m), F-6, F-8 −125.7, −131.7 (4F, AB pattern), F-7 −114.1, −137.4 (2F, AB pattern), δ ^{31}P 130.1 (sep,q); $^2J_{F6,F8} = 271.8$, $^2J_{F7} = 275.8$, $^3J_{P-H} = 10.19$, $^7J_{H-F7(axial)} = 3.36$, $^4J_{P-CF3} = 14.2$ Hz; MS of mixture [EI] *m/e* 422 (7.3, M^+), 391 (1.4, $M-OCH_3^+$), 275 (1.5, $CF_2CF_2(O)(CF_3)COPOCH_3^+$), 247 (2.4, $CF_3(O)CCF_2CF_2CF_2^+$), 225 (7.5, $CF_2(O)(CF_3)COPOCH_3^+$), 197 (2.1, $CF_3(O)CCF_2CF_2^+$), 181 (2.8, $C_4F_9^+$), 175 (21.9, $O(CF_3)COPOCH_3^+$), 169 (12.1, $C_3F_7^+$), 147 (3.5, $CF3(O)CCF_2^+$), 131 (16.4, $C_3F_5^+$), 109 (11.3, CF_2COP^+), 100 (12.2, $C_2F_4^+$), 97 (13.9, CF_3CO^+), 81 (100.0, CF_3C^+), 78 (69.9, $OPOCH_3^+$), 69 (79.7, CF_3^+), 62 (4.2, $POCH_3^+$), 50 (9.8, CF_2^+), 47 (24.2, PO^+); [CI] *m/e* 423 (100.0, MH^+), 403 (27.2, $MH-HF^+$), 391 (2.9, $MH-CH_3OH^+$), 359 (2.5, $MH-CH_3OH-O_2^+$), 275 (1.1, $CF_2CF_2(O)(CF_3)COPOCH_3^+$), 225 (3.6, $CF_2(O)(CF_3)COPOCH_3^+$), 175 (4.3, $O(CF_3)COPOCH_3^+$), 131 (1.7, $CF_3CCF_2^+$), 125 (1.9, CF_3COCO^+).

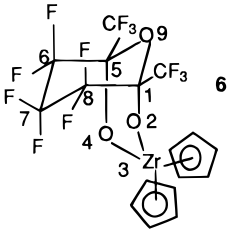
Reaction of 1 with $(C_5H_5)_2TiCl_2$. Into a 100 mL reactor was added 0.19 g, 0.76 mmol, of titanocene dichloride and 0.32 g, 0.79 mmol, of the alkoxide **1**. The flask was evacuated, and 7 mL of toluene was added to the reactor via syringe. The flask was stirred for 16 h at 25 °C. The toluene was removed under high vacuum leaving a light green residue. The residue was collected and vacuum sublimated at 110 °C to yield 3,3-bis(η^5-cyclopentadienyl)-1,5-bis(trifluoromethyl)-6,6,7,7,8,8-hexafluoro-2,4,9-trioxa-3-titanabicyclo[3.3.1]nonane (**5**) (0.15 g, 37% yield), a green solid.



5

The titanocene alkoxide **5** was characterized as follows: IR (KBr) 3123 (w), 3064 (w), 2943 (w), 1435 (w), 1342 (m), 1286 (s), 1256 (s), 1193 (vs), 1151 (s), 1122 (s), 1041 (s), 1022 (s), 1000 (s), 913 (s), 827 (vs), 760 (vw), 740 (vw), 684 (w), 664 (w), 645 (w), 615 (m), 508 (w) cm^{-1}; NMR ($CDCl_3$, 24 °C) δ ^{1}H 6.61 (5H, s), 6.60 (5H, d), δ ^{19}F CF_3 −77.5 (6F, m), F-6, F-8 −123.6, −128.3 (4F, AB pattern), F-7 −115.7, −136.7 (2F, AB pattern); $^2J_{F6,F8} = 263.6$, $^2J_{F7} = 272.2$, $^7J_{F7(axial)C5H5} = 1.82$ Hz; MS ^{48}Ti [CI] *m/e* 539 (25.4, MH^+), 473 (25.4, $MH-C_5H_5^+$), 197 (100.0, $CF_3COCF_2CF_2^+$), 195 (60.3, $(C_5H_5)_2TiOH^+$), 151 (65.1, $C_3F_6H^+$), 132 (46.0, $C_3F_5H^+$), 129 (42.9, $C_3F_4OH^+$).

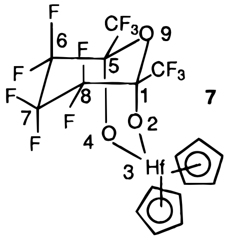
Reaction of 1 with $(C_5H_5)_2ZrCl_2$. To a 100 mL reactor were added **1** (0.34 g, 0.84 mmol) and zirconocene dichloride (0.23 g, 0.79 mmol). The reactor was evacuated, and dry toluene (7 mL) was added by vacuum transfer. The mixture was stirred for 15 h at 25 °C. The toluene was removed under high vacuum leaving a light yellow solid. The solid was collected and sublimed at 135 °C to yield 3,3-bis(η^5-cyclopentadienyl)-1,5-bis(trifluoromethyl)-6,6,7,7,8,8-hexafluoro-2,4,9-trioxa-3-zirconabicyclo[3.3.1]nonane (**6**) (0.20 g, 44% yield) as an off-white solid. **6** was readily soluble in chloroform and dichloromethane.



6

The zirconocene alkoxide **6** was characterized as follows: IR (KBr) 3096 (w), 3057 (vw), 1433 (w), 1345 (m), 1314 (m), 1286 (s), 1264 (m), 1204 (vs), 1188 (vs), 1181 (vs), 1154 (s), 1137 (m), 1125 (s), 1072 (m), 1039 (m), 1017 (s), 1006 (s), 912 (s), 818 (vs), 760 (vw), 739 (w), 685 (vw), 669 (w), 646 (w), 615 (w), 594 (w), 553 (w), 505 (w) cm^{-1}; NMR ($CDCl_3$, 24 °C) δ ^{1}H 6.57 (5H, s), 6.55 (5H, d), δ ^{19}F CF_3 −78.9 (6F, m), F-6, F-8 −125.3, −129.7 (4F, AB pattern), F-7 −114.9, −138.5 (2F, AB pattern); $^2J_{F6,F8} = 266.1$, $^2J_{F7} = 274.7$, $^7J_{F7(axial)C5H5} = 1.78$ Hz; MS ^{90}Zr [EI] *m/e* 580 (9.1, M^+), 333 (9.5, $(C_5H_5)_2ZrOC(CF_3)O^+$), 239 (33.5, $(C_5H_5)_2ZrF^+$), 197 (22.7, $CF_3C(O)CF_2CF_2^+$), 193 (100.0, $(C_5H_5)C(O)CF_2CF_2^+$), 171 (10.2, $(C_5H_5)ZrO^+$), 147 (10.3, $CF_3C(O)CF_2^+$), 131 (10.7, $C_3F_5^+$), 97 (10.6, CF_3CO^+), 69 (11.8, CF_3^+), 65 (9.2, $C_5H_5^+$).

Reaction of 1 with $(C_5H_5)_2HfCl_2$. The procedure used for preparing **6** was followed using a 100 mL reactor, hafnocene dichloride **1** (0.33 g, 0.81 mmol), (0.30 g, 0.79 mmol), and toluene (7 mL). Sublimation at 135 °C yielded 3,3-bis(η5-cyclopentadienyl)-1,5-bis(trifluoromethyl)-6,6,7,7,8,8-hexafluoro-2,4,9-trioxa-3-hafnabicylo[3.3.1]nonane (**7**) (0.33 g, 62% yield), an off-white solid.



7

The hafnocene alkoxide **7** was characterized as follows: IR (KBr) 3129 (vw), 3089 (vw), 1357 (w),1326 (w), 1298 (s), 1276 (m), 1217 (vs), 1198 (vs), 1164 (s), 1148 (m), 1136 (s), 1080 (w), 1050 (m), 1017 (s), 921 (s), 830 (vs), 743 (w), 675 (w), 647 (vw), 621 (w), 577 (w), 537 (w), 523 (w), 434 (w) cm^{-1}; NMR ($CDCl_3$, 24 °C) δ ^{1}H 6.50 (5H, s), 6.48 (5H, d), δ ^{19}F CF_3 −78.9 (6F, m), F-6, F-8 −125.17, −129.5 (4F, AB pattern), F-7 −114.9, −138.2 (2F, AB pattern); $^2J_{F6,F8} = 265.2$, $^2J_{F7} = 274.8$, $^7J_{F7(axial)C5H5} = 1.83$ Hz; MS ^{177}Hf [EI] *m/e* 667 (7.9, M^+), 420 (20.0, $(C_5H_5)_2HfOC(CF_3)O^+$), 326 (63.6, $(C_5H_5)HfOCOCOC^+$), 247 (45.5, $CF_3COCF_2CF_2CF_2^+$), 197 (38.8, $CF_3COCF_2CF_2^+$), 169 (83.6, $C_3F_7^+$), 131 (49.7, $C_3F_5^+$), 109 (27.3, CF_3COC^+), 97 (93.9, CF_3CO^+), 69 (100.0, CF_3^+), 65 (78.8, $C_5H_5^+$).

Reaction of 1 with $[CF_3C(O)]_2O$. **1** (0.32 g, 0.79 mmol) was added to a 100 mL reactor. Dry sulfolane (2 mL) was added to the reactor which was then cooled to −196 °C and evacuated. Trifluoroacetic anhydride (1.45 mmol) was added to the reactor by vacuum transfer. The reactor was then stirred for 4 h at 25 °C and stirred for 1 h at 90 °C. The volatile materials were removed under vacuum through traps at −18, −54, and −196 °C. The −54 °C trap contained 0.31 mmol of material determined by ^{19}F NMR to consist of (mol %) $CF_3(O)C(CF_2)_3C(O)CF_3$ (93) and TFAA (7). Additional material (0.91 mmol) was collected in the −196 °C trap and consisted of (mol %) TFAA (51) and $CF_3(O)C(CF_2)_3C(O)CF_3$ (49). Total recovery of the diketone was 94% while the amount of TFAA recovered corresponded to a 71% conversion. ^{19}F NMR of the reactor solvent in CD_3CN gave only a singlet at −75.0 ppm, confirming the presence of $CF_3COO^-Na^+$.

Reaction of 1 with $CH_3C(O)F$. The disodium alkoxide (0.27 g, 0.67 mmol) and a magnetic stirring bar were added to a 100 mL reactor. Dry sulfolane (2 mL) was added to the reactor, which was then cooled to −196 °C and evacuated. Acetyl fluoride (1.50 mmol) was added to the reactor by vacuum transfer. The reactor was stirred for 12 h at 60 °C. The volatiles were pumped off and fractionated through traps at −69 and −196 °C. The −196 ° trap contained 0.33 mol of $CH_3C(O)F$. Fractionation of the −69 °C trap through traps at −22 and −196 °C gave 0.39 mmol (58% recovery) of $CF_3(O)C(CF_2)_3C(O)CF_3$.

Reaction of 1 with SO_2Cl_2. A 25 mL reactor was loaded with acridine (0.60 g, 3.3 mmol) and **1** (0.34 g, 0.84 mmol). The mixture was then stirred at 25 °C for 3 h. The flask was then evacuated and cooled to −196 °C. Sulfuryl chloride (0.75 mmol) and CH_2Cl_2 (31.20 mmol) were added by vacuum transfer. The reaction mixture was placed in an ice bath at 0 °C with stirring and allowed to warm to 20 °C over 24 h. The volatile materials were removed under vacuum through traps at −35 and −196 °C. The −196 °C trap was found to contain 32.58 mmol of material which was determined to be a mixture of CH_2Cl_2 and $CF_3(O)C(CF_2)_3C(O)CF_3$ by IR.

A Beer's law plot of the absorbance of the diketone at 1797.5 cm^{-1} ($\nu_{C=O}$) versus vapor pressure (Torr) was made in an effort to estimate the amount of diketone obtained. A linear regression analysis indicated that the amount of $CF_3(O)C(CF_2)_3C(O)CF_3$ recovered was ca. 100%.

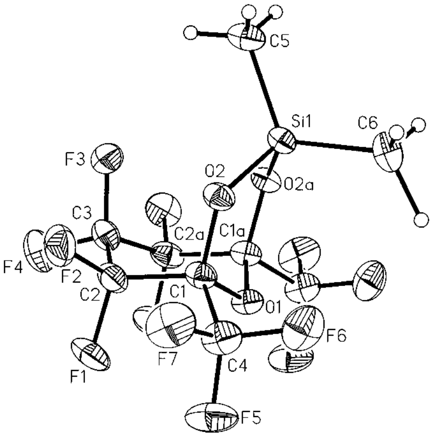


Figure 1. Thermal ellipsoid plot of **3** (50% probability) showing the atom numbering scheme used.

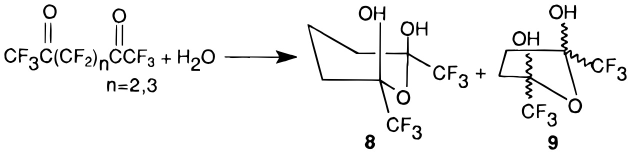
Attempted Reaction of 1 with CF_2=CF_2. Reaction of **1** with excess C_2F_4 at 75 °C in THF showed no change after 5 h and complete recovery of the C_2F_4.

Attempted Reaction of 1 with 1,2-Dichlorotetrafluorocyclobutene-1. After 14 h at 75 °C in CH_3CN, **1** showed no reaction with the cyclobutene.

Results and Discussion

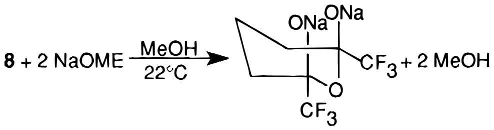
Perfluorinated alkoxides as ligands are very limited due to the fact that precursor alcohols are only stable if they contain no alpha fluorine atoms. Thus perfluoropinacol and perfluoro-*tert*-butyl alcohol represent the only well-studied cases. Improved methods have been developed for the synthesis of a variety of perfluorotertiary alcohols,[8] but they have not been well studied. Perfluorinated alkoxide anions can be generated from the respective epoxides, ketones, and acid fluorides *in situ* by reaction with metal fluorides in polar solvents.[9] However, it has not been possible to use the oxyanions generated in this manner as general synthons, and their application has been mainly restricted to the synthesis of fluorocarbon ethers.

The recent synthesis of novel cyclic diols by reaction of water with the diketones[7] provided an opportunity to extend the chemistry of perfluorinated alkoxides.



8 **9**

Since compound **8** is formed exclusively as the *cis* isomer, whereas **9** is always a mixture of *cis* and *trans* isomers, we chose to investigate **8** to avoid obvious complications that would occur in the chemistry of **9**. The pk_1 of **8** is 5.4, and the desired alkoxide derivative **1** was easily prepared by reaction with NaOMe.

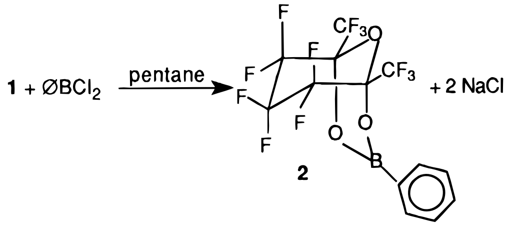


1

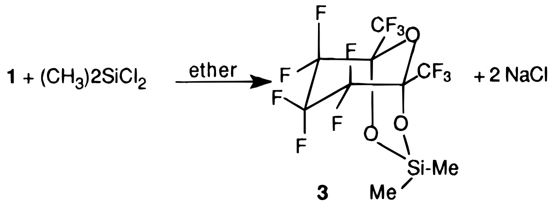
Compound **1** is a stable white solid which is readily soluble in a variety of solvents such as acetonitrile, acetone, and alcohol.

We expected that **1** would react readily with a variety of dichloro compounds to yield novel bicyclic heterocycles containing a six-membered trioxo ring. In general the chemistry parallels that of the lithium and sodium alkoxide derivatives of perfluoropinacol, but some analogous reactions failed. If the substrate contained more than two replaceable chlorines, polymeric materials were formed. The reactions described herein represent a limited survey of the reaction chemistry. Clearly the reactions described can be extended to many analogues and other new substrates.

The reaction of **1** with phenylboron dichloride in pentane or dimethyldichlorosilane in ether gave immediate formation of solid NaCl and the respective bicyclic heterocycles.



2

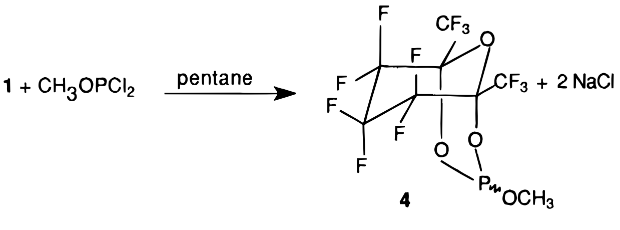


3

Compounds **2** and **3** are well characterized by the data in the Experimental Section. From the ^{19}F NMR results it is clear that the basic ring conformation of the original alkoxide is maintained with equivalent *cis*-CF_3 groups and two types of CF_2 groups with magnetically nonequivalent axial and equitorial fluorines. For **3**, the trioxosilane ring clearly has one methyl group in close proximity to the axial fluorine at C-7, resulting in a $^7J_{HF}$ coupling of 2.0 Hz. The confirmation of the bicyclic rings in **3** (and probably in all cases) was confirmed by a single crystal X-ray structure.

A thermal ellipsoid plot of **3** is shown in Figure 1. The compound crystallizes in the orthorhombic space group, *Pnma* (No. 62), with four molecules per unit cell; the molecule is bisected by a crystallographic mirror plane (*x, 3/4, z*) coincident with atoms Si(1), F(3), F(4), O(1), C(3), C(6), and C(5). All distances and angles for this compound fall within accepted norms, and there were no unusual packing interactions; selected bond distance and angle information is given in Table 2. The structure clearly shows that the trioxo ring adopts a boat confirmation, whereas the oxacyclohexane ring is the expected chair conformation. The distance from the axial fluorine at C-7 (C(3) in Figure 1) to the hydrogen atoms of the nearest methyl group is 2.70(5) Å. This close approach can account for the observed through space coupling.

The reaction of **1** with methyl dichlorophosphite in pentane gives the trioxophosphane in excellent yield.



4

Compound **4** as isolated is a mixture of *exo* and *endo* (51:49) isomers at phosphorus. This is clearly evident from the ^{19}F

---

(8) Kotun, S. P.; Anderson, J. D. O.; DesMarteau, D. D. *J. Org. Chem.* **1992**, *57*, 1124.

(9) Chambers, R. D. *Fluorine in Organic Chemistry*; Wiley Interscience: New York; 1973.

Table 2. Bond Distances (Å) and Angles (deg) for **3**[a]

Distances

Si(1)−O(2)	1.672(1)	Si(1)−C(5)	1.829(4)
Si(1)−C(6)	1.830(4)	F(1)−C(2)	1.354(3)
F(2)−C(2)	1.336(3)	F(3)−C(3)	1.350(4)
F(4)−C(3)	1.344(4)	F(5)−C(4)	1.328(3)
F(6)−C(4)	1.319(3)	F(7)−C(4)	1.327(3)
O(1)−C(1)	1.421(2)	O(2)−C(1)	1.369(2)
C(1)−C(2)	1.552(3)	C(1)−C(4)	1.544(3)
C(2)−C(3)	1.535(3)		

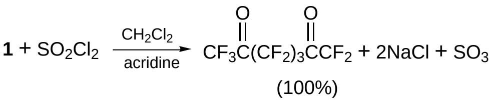
Angles

O(2)−Si(1)−C(5)	109.1(1)	O(2)−Si(1)−C(6)	111.2(1)
C(5)−Si(1)−C(6)	114.6(2)	O(2)−Si(1)−O(2a)	100.7(1)
C(1)−O(1)−C(1a)	115.2(2)	Si(1)−O(2)−C(1)	122.1(1)
O(1)−C(1)−O(2)	114.2(2)	O(1)−C(1)−C(2)	107.8(2)
O(2)−C(1)−C(2)	108.9(2)	O(1)−C(1)−C(4)	103.9(2)
O(2)−C(1)−C(4)	108.3(2)	C(2)−C(1)−C(4)	113.8(2)
F(1)−C(2)−F(2)	107.5(2)	F(1)−C(2)−C(1)	109.8(2)
F(2)−C(2)−C(1)	111.1(2)	F(1)−C(2)−C(3)	107.4(2)
F(2)−C(2)−C(3)	109.4(2)	C(1)−C(2)−C(3)	111.4(2)
F(3)−C(3)−F(4)	106.6(2)	F(3)−C(3)−C(2)	108.8(2)
F(4)−C(3)−C(2)	109.5(2)	C(2)−C(3)−C(2a)	113.4(3)
F(5)−C(4)−F(6)	108.0(2)	F(5)−C(4)−F(7)	107.9(2)
F(6)−C(4)−F(7)	108.4(2)	F(5)−C(4)−C(1)	112.7(2)
F(6)−C(4)−C(1)	109.6(2)	F(7)−C(4)−C(1)	110.1(2)

[a] Atoms labeled with a lower-case character were generated by the following symmetry operation: (a) *x*, $^3/_2 - y$, *z*.

NMR data and the $^7J_{H-F}$ coupling of the axial fluorine at C-7 to the *endo* methyl group. This ^7J coupling is not observed in the *exo* isomer. The isomerization at phosphorus from *endo* to *exo* was apparent on standing in $CDCl_3$ (70:30 after 24 h). Addition of a trace of methanol greatly increased the rate of isomerization to the *exo* isomer. Similar results have been observed for related six-membered ring phosphites.[10] The observed isomer ratio in the isolated **4** may depend on the presence of traces of methanol in the starting alkoxide **1**, but this was not investigated.

The reaction of **1** with pure SO_2Cl_2 in CH_2Cl_2 in the presence of acridine to remove any HCl present in SO_2Cl_2 did not give the expected cyclic sulfate as was observed with sodium pinacolate.

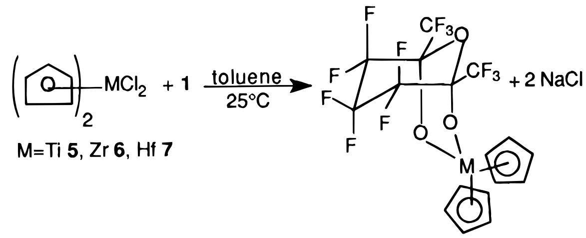


$$\mathbf{1} + SO_2Cl_2 \xrightarrow[\text{acridine}]{CH_2Cl_2} CF_3\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}CF_2 + 2NaCl + SO_3$$

(100%)

The formation of SO_3 was not confirmed but is reasonable, and it would be complexed by the acridine. It is possible that the latter assists in the decomposition of the cyclic sulfate, but we did not observe the expected product in the absence of base.

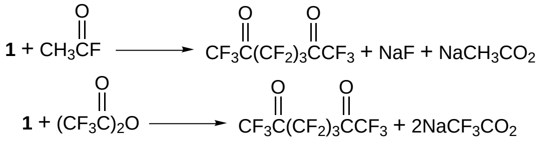
Reaction of 1 with Group 4 Dichlorides. There are few reports of partially fluorinated alkoxides of transition metals[11] and very few examples of fluorine-containing metallocine alkoxides.[12] Partially fluorinated alkoxides are important in the reactivity of olefin metathesis catalysts of tungsten and molybdenum.[13] It was therefore of interest to look at **1** as a source of perfluoroalkoxide derivatives of transition metals. For this purpose we chose the readily available metallocene dichlorides of Group 4. Reaction with **1** in toluene gave good to moderate yields of the respective bicyclic heterocycles.



Compounds **5**−**7** were readily soluble in dichloromethane and chloroform. Above 100 °C, all could be easily sublimed under vacuum. While the zirconium and hafnium alkoxides are white, the titanium alkoxide was green in color. The UV spectrum of the titanium alkoxide in CH_2Cl_2 exhibited a strong absorption band at 255 nm (ϵ_{max} 19 300). The exact reason for this color has not been determined, but ligand to metal charge transfer may be responsible. Another interesting feature of these alkoxides is the apparent through space coupling of the axial fluorine at C-7 with one of the cyclopentadienyl rings attached to the metal. Coupling in all three cases is on the order of 1.8 Hz and was confirmed by decoupling experiments. Mass spectra showed molecular peaks for all three alkoxides indicating that these compounds are monomeric in the vapor state. All of the alkoxides are moisture sensitive and perhaps are oxygen sensitive as well, as evidenced by their discoloration in a nitrogen-filled drybox after a few days.

Other Reactions of 1. Attempts were made to use **1** in the nucleophilic substitution of the fluorinated alkenes C_2F_4 and 1,2-dichlorotetrafluorocyclobutene. Both of these alkenes react with a variety of nucleophiles,[9] but the nucleopilicity of **1** was too low, and no reaction was observed under favorable conditions. The incorporation of this ring system into vinyl ether monomers is of interest on the basis of the unusual properties of polymers such as Teflon AF and related polymers obtained from cyclopolymerization of fluorinated divinyl ethers and polymerization of 1,3-dioxoles.[14]

Compound **1** was sufficiently nucleophilic to react with $CH_3C(O)F$ and $[CF_3C(O)]_2O$. Unfortunately the respective esters were unstable.



$$\mathbf{1} + CH_3\overset{O}{\overset{\|}{C}}F \longrightarrow CF_3\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}CF_3 + NaF + NaCH_3CO_2$$

$$\mathbf{1} + (CF_3\overset{O}{\overset{\|}{C}})_2O \longrightarrow CF_3\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}CF_3 + 2NaCF_3CO_2$$

Fluorinated esters are unstable in the presence of strong fluoride sources, but sodium fluoride is normally not sufficiently active to cause decomposition.[15]

$$R_f\overset{O}{\overset{\|}{C}}ORf \xrightarrow{F^-} R_f\overset{O}{\overset{\|}{C}}F + R_f'\overset{O}{\overset{\|}{C}}F$$

The observed products suggest that a common intermediate is

---

[10] Denney, D. Z.; Denney, D. B. *J. Am. Chem. Soc.* **1966**, *88*, 1830.

[11] Mazdiyasni, K. S.; Schaper, B. J.; Brown, L. M. *Inorg. Chem.* **1971**, *10*, 889.

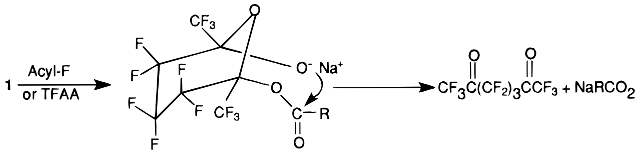
[12] Drozdov, G. V.; Klebanskii, A. L.; Bartashev, V. A. *Zh. Obshch.Khim. USSR (Engl. Transl.)* **1963**, *33*, 2362. Basso, B. M.; Gervais, D. *Inorg. Chim. Acta* **1979**, *34*, 191.

[13] Schaverien, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2771. Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423. Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L.; Dilmare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Kruger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262. Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

[14] Resnick, P. R. U. S. Patent 3 865 845, 1975. Resnick, P. R. U. S. Patent 3 978 030, 1976. Resnick, P. R. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **1990**, *31*, 312. Hung, M.-H.; Resnick, P. R. *J. Am. Chem. Soc.* **1990**, *112*, 9671.

[15] Tari I.; DesMarteau, D. D. *J. Org. Chem.* **1980**, *45*, 1214.

involved in the above reactions. The monoester is probably formed followed by an internal nucleophilic attack of the alkoxide function on the ester. The loss of the acetate group then leads to the ring opening and the ketone.



The desired esters might be isolable using a large excess of the acyl fluoride or anhydride, but this was not attempted.

Conclusion

The novel disodium alkoxide **1** provides a route to unusual bicyclic heterocycles by reaction with dichlorides of metals and nonmetals. The examples presented represent only a limited survey of the reactivity of **1** but serve to establish its similarity to the reactivity of perfluoropinacolates. The molecular structure obtained for the product **3** with $(CH_3)_2SiCl_2$ indicates that the trioxo ring adopts a boat conformation with the oxacyclohexane ring having a chair confirmation. This places one of the methyl groups on silicon in juxtaposition with an axial fluorine at C-7 giving rise to an apparent $^7J_{HF}$ coupling via through space interaction. Observations of related long-range coupling in several other derivatives suggest that the basic structure observed for **3** is common to all the bicyclic derivatives.

Acknowledgment. The financial support of this research by Ausimont, SpA, and support of the X-ray structure facilities by the National Science Foundation is gratefully acknowledged.

Supporting Information Available: Complete listings for **3** of crystallographic data, atomic coordinates, bonding distances and angles, and anisotropic thermal parameters (4 pages). Ordering information is given on any current masthead page.

IC9508435