New Titanatranes and an Unexpected Reactivity Trend in (Dialkylamido)titanatranes†

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The relative rates of displacement of the NR_2 group in (dialkylamido)titanatranes $R_2NTi(OCH_2CH_2)_3N$ by –OH and –SH compounds is in the order $NEt_2 >> NMe_2 > N(i\text{-}Pr)_2$. This unanticipated order is rationalized on the postulated prior formation of $HR_2N^+Ti(OCH_2CH_2)_3N$ (**A**), which facilitates departure of R_2NH upon subsequent nucleophilic attack. For R = Et and *i*-Pr, the concentration of **A** is higher than for R = Me, owing to the basicity order $Et_2N \cong (i\text{-}Pr)_2N > Me_2N$. The greater reactivity of **A** where R = Me relative to R = *i*-Pr is attributed to the greater steric protection from nucleophilic attack on the metal afforded by the $H(i\text{-}Pr)_2N^+$ group. The faster reactions of CF_3CH_2OH and PhOH compared with their sterically similar but more weakly acidic analogues CH_3CH_2OH and *i*-PrOH, respectively, support this hypothesis as do the comparable displacement rates of Et_2N and Me_2N in the presence of the strong nonnucleophilic base $P(MeNCH_2CH_2)_3N$ and the reactions of **4** and **14** with HBF_4 and NH_4Cl but not with $NaBF_4$ or Me_4NCl. New titanatranyl derivatives reported include five arylates, two thioarylates, and four diolates. The X-ray parameters for $[i\text{-}PrSTi(OCH_2CH_2)_3N]_2$ are as follows: triclinic, space group $P\bar{1}$ (No. 2), a = 7.434(5) Å, b = 12.540(3) Å, c = 7.034(3) Å, α = 105.72(3)°, β = 98.87(3)°, γ = 85.30(4)°, and Z = 1. For $[Me_2COTi(OCH_2CH_2)_3N]_2$ these parameters are as follows: monoclinic, space group $P2_1/n$ (No. 14), a = 6.6590(6) Å, b = 17.819(2) Å, c = 10.095(1) Å, and β = 107.975(9)°.

Introduction

Titanatranes offer the opportunity to investigate single substitution reactions on Ti(IV) esters and amides. Whereas normal four-coordinate compounds of the latter type (i.e., $Ti(OR)_4$ and $Ti(NR_2)_4$) are prone to multiple substitutions by nucleophiles, titanatranes are more robust to displacements beyond that of the axial substituent, owing to the stability of the tricyclic framework. Earlier we showed that the Cp group in **1** (Chart I) is displaced by alcohols, phenol, Ph_3SiOH and HOAc (but not by amides) and that the OR groups in **2** and **3** are displaced by PhOH, Ph_3SiOH and HOAc.[1] More recently we demonstrated that the NMe_2 group in **4** is displaced by a variety of –OH compounds to give **2**, **3** and **5–7**, and by –SH compounds to give **8–12**.[2] It has also been observed that the Cp group displaces the chloride from **13**.[3]

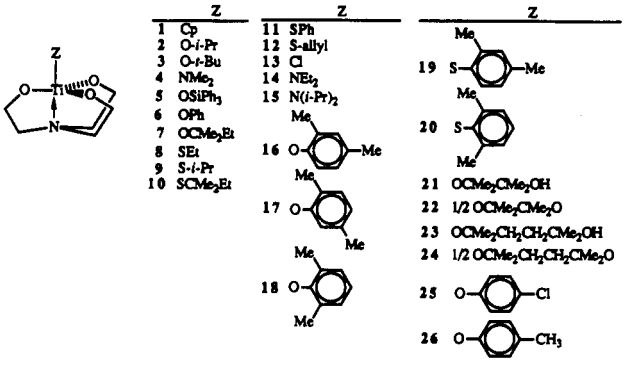
Here we report that the relative rates of displacement of NMe_2, NEt_2 and $N(i\text{-}Pr)_2$ from **4**, **14** and **15**, respectively, by –OH and –SH compounds is curiously in the general order **14 >> 4 > 15**, for which a rationale based on the relative basicities and steric properties of the NR_2 substituent is suggested. We also describe the preparation of the new compounds **14–26** and the molecular structures of **9** and **22** by X-ray means.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of prepurified argon or nitrogen at room temperature using standard inert-atmosphere and Schlenk techniques.[4] Tetrahydrofuran, pentane and toluene were distilled from Na/benzophenone under nitrogen. *tert*-Butyl alcohol was distilled from Na and dichloromethane, and acetonitrile was distilled from calcium hydride under argon. Ethyl alcohol was distilled from Mg activated by a small amount of iodine.

^1H, ^{13}C and ^{19}F NMR spectra were recorded on a Nicolet NT-300 or a Varian VXR-300 spectrometer in $CDCl_3$, CD_3CN or C_6D_6, using the proton impurity of the solvents as an internal reference for the ^1H spectra, the ^{13}C resonance of the solvents as a reference for ^{13}C spectra, and hexafluoro benzene (external reference) for ^{19}F NMR spectra. Variable temperature ^1H, ^{13}C and ^{19}F NMR spectra were run on a Bruker WM-200 or a Varian VXR-300 instrument. Mass spectra were obtained on a Finnigan 4000 instrument or a Kratos MS-50 spectrometer. FT-IR spectra were recorded on an IBM-IR98 spectrophotometer as Nujol mulls. Melting points were determined with a Thomas Hoover capillary apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. The strong base $P(MeNCH_2CH_2)_3N$ was synthesized according to the literature procedure.[5]

Chart I



Preparation of $Ti(NMe_2)_4$ and $Ti(NEt_2)_4$. The procedure reported by Bradley and Thomas was used,[6] except that $TiCl_4(THF)_2$ was employed instead of $TiCl_4$, and the reaction was carried out at room temperature.

$Ti(NMe_2)_4$: Yield 87%, yellow oil; bp, 35–37 °C at 0.04 mmHg; ^1H NMR (C_6D_6) δ 3.10 (s, 12 H, CH_3); ^{13}C NMR (C_6D_6) δ 44.00 (CH_3); MS m/e (relative intensity) 225 (21, M^+), 224 (100, M^+) 223 (M^+) 181 (36, $M^+ - NMe_2$) 180 (17, $M^+ - NMe_2$) 179 (53) 137 (3, $M^+ - 2NMe_2$) 136 (6, $M^+ - 2NMe_2$) 135 (12) 93 (10, $M^+ - 3NMe_2$) 92 (31, $M^+ - 3NMe_2$) 91 (57); IR (KBr, neat) 2955, 2926, 2812, 2716, 2505, 2293, 2152, 2091, 1539, 1452, 1250, 1151, 1121, 1055, 942 cm^{-1}.

$Ti(NEt_2)_4$: Yield, 71%, orange oil; bp, 93–95 °C at 0.04 mmHg; ^1H NMR (C_6D_6) δ 0.99 (t, 12 H, $^3J_{H-H}$ = 6.9 Hz, CH_3) 3.58 (q, 8H, $^3J_{H-H}$

† Dedicated to the memory of the late Carl H. Brubaker.

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= 6.9 Hz, CH_2); ^{13}C NMR (C_6D_6) δ 15.6 (CH_2CH_3) 45.34 (CH_2CH_3); MS, *m/e* (relative intensity) 336 (33, M^+) 335 (5, M^+) 264 (20, $M^+ - NEt_2$) 263 (69, $M^+ - NEt_2$) 192 (3, $M^+ - 2NEt_2$) 191 (5, $M^+ - 2NEt_2$) 120 (6, $M^+ - 3NEt_2$) 119 (13, $M^+ - 3NEt_2$); IR (KBr, neat) 2958, 2851, 2666, 2598, 2359, 1457, 1447, 1366, 1332, 1104, 1093, 1001, 800, 790, 721, 667, 608 cm^{-1}.

Preparation of (Diethylamino)titanatrane (14). To a solution of 2.8 g (8.3 mmol) of $Ti(NEt_2)_4$ in 125 mL of dry THF, cooled to 0 °C, was added 1.11 mL (1.24 g, 8.34 mmol, of triethanol amine (TEA). After the reaction flask was stirred for 6 h at room temperature, the solvent was removed under vacuum and the remaining fine yellow solid dissolved in ca. 50 mL of dry CH_2Cl_2 and layered with pentane. Small yellow crystals appeared after several days. Yield, 1.8 g (82%); mp, 215–217 °C (dec); ^1H NMR ($CDCl_3$) δ 0.95 (t, 12 H, $^3J_{H-H}$ = 6.9 Hz, CH_2CH_3) 2.79 (6, 4 H, $^3J_{H-H}$ = 5.7 Hz, NCH_2) 3.00–3.51 (m, 8 H, NCH_2), 3.71 (q, 8 H, $^3J_{H-H}$ = 6.9 Hz, CH_2CH_3) 4.29 (t, 4 H, $^3J_{H-H}$ = 5.7 Hz, OCH_2), 4.39–4.74 (m, 8 H, OCH_2); ^1H NMR (300 MHz, CD_3CN) δ 1.01 (t, 6 H, $^3J_{H-H}$ = 7.2 Hz, CH_2CH_3) 2.84 (t, 4 H, $^3J_{H-H}$ = 5.7 Hz, NCH_2) 2.98–3.25 (m, 8 H, NCH_2) 3.67 (q, 4 H, $^3J_{H-H}$ = 7.2 Hz, CH_2CH_3) 4.18 (t, 4 H, $^3J_{H-H}$ = 5.7 Hz, OCH_2) 4.34–4.41 (m, 4 H, OCH_2) 4.55–4.64 (m, 4 H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 16.53 (CH_2CH_3) 51.84 (CH_2CH_3) 57.66 (CH_2N), 64.03 (2 C, CH_2N) 71.33 (CH_2O) 72.37 (2 C, CH_2O); MS *m/e* (relative intensity) 267 (4, M^+) 266 (3, M^+) 265 (4, M^+) 264 (4) 263 (4) 252 (3, M^+ – Me) 251 (7, M^+ – Me) 250 (4) 238 (6, M^+ – Et) 237 (16, M^+ – Et) 236 (7) 235 (4) 208 (7, M^+ – 2Et) 207 (20, M^+ – 2Et) 206 (10) 205 (8) 195 (10, $M^+ - NEt_2$) 194 (48, $M^+ - NEt_2$) 193 (9) 192 (9) 167 (4, $M^+ - NEt_2 - CH_2CH_2$) 166 (6, $M^+ - NEt_2 - CH_2CH_2$) 165 (11) 164 (22).

Preparation of (Diisopropylamino)titanatrane (15). Compound **14** (0.8 g, 3.0 mmol) was dissolved in 25 mL of diisopropylamine. The reaction mixture was refluxed for 24 h followed by solvent removal under vacuum. Although the ^1H NMR spectrum of the yellow product showed that **14** converted to **15** quantitatively, the yield of **15** after crystallization from CH_2Cl_2/pentane was 61%; mp, 170–172 °C; ^1H NMR (CD_3CN) δ 1.15 (d, 12 H, $NCH(CH_3)_2$ $^3J_{H-H}$ = 6.3 Hz) 3.12 (m, 6 H, NCH_2) 3.65 (h, 2 H, $NCHMe_2$, $^3J_{H-H}$ = 6.3 Hz) 4.36 (m, 6 H, OCH_2); ^1H NMR ($CDCl_3$) δ 1.19 (d, 12 H, $NCH(CH_3)_2$, $^3J_{H-H}$ = 6.3 Hz) 3.15 (m, 6 H, NCH_2) 3.61 (h, 2 H, $NCHMe_2$, $^3J_{H-H}$ = 6.3 Hz) 4.42 (m, 6 H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 23.4 ($NCH(CH_3)_2$) 58.9 ($NCHMe_2$) 59.4 (NCH_2) 71.7 (OCH_2); MS *m/e* (relative intensity) 294 (5, M^+) 293 (4, M^+) 292 (10) 254 (5, M^+ – *i*-Pr) 250 (3) 208 (13, M^+ – *i*-Pr) 207 (12, M^+ – *i*-Pr) 194 (21, $M^+ - N(i\text{-}Pr)_2$) 193 (17).

Preparation of (2,4-Dimethylphenolato)titanatrane (16). In a 100 mL round bottom flask equipped with a side arm, (diethylamino)-titanatrane **14** (0.10 g, 0.38 mmol was dissolved in 15 mL of dry CH_2Cl_2 and 60 μL (58.4 mg, 0.48 mmol) of 2,4-dimethylphenol was added. After allowing the solution to stir for 2 h, it was layered with pentane. Yellow crystals separated which were dried under vacuum. Yield 83%; mp, 147–149 °C (dec); ^1H NMR ($CDCl_3$) δ 2.18 (S, 6 H, CH_3) 3.25 (t, 6 H, $^3J_{H-H}$ 5.4 Hz, NCH_2) 4.53 (t, 6 H, $^3J_{H-H}$ = 5.4 Hz, OCH_2) 6.78–6.84 (m, 3 H, C_6H_3); ^{13}C NMR ($CDCl_3$) δ, 20.51 (CH_3) 58.71 (NCH_2) 77.8 (OCH_2) 127.05, 127.10, 127.16, 127.18, 129.39, 131.23 (C_6H_3); MS (*m/e*, relative intensity) 316 (19, M^+) 315 (84, M^+) 314 (12) 285 (5, M^+ – 2Me) 210 (3, $M^+ - C_8H_9$) 194 (11, $M^+ - OC_8H_9$).

Preparation of (2,5-Dimethylphenolato)titanatrane (17). The procedure was the same as for **16** except that 46 mg (0.38 mmol) of 2,5-dimethylphenol was used. Yield, 89%; mp, 65–67 °C (dec); ^1H NMR ($CDCl_3$) δ 2.20 (s, 3 H, CH_3) 2.30 (s, 3 H, CH_3) 3.27 (t, 6 H, $^3J_{H-H}$ = 5.4 Hz, NCH_2) 4.53 (t, 6 H, $^3J_{H-H}$ = 5.4 Hz, OCH_2) 6.53–6.92 (m, 3 H, C_6H_3); ^{13}C NMR ($CDCl_3$) δ 20.96 (CH_3) 58.02 (NCH_2) 71.67 (OCH_2) 119.92, 121.00, 129.65, 129.67, 129.68, 129.75, (C_6H_3); MS, *m/e* (relative intensity) 316 (22, M^+) 315 (100, M^+) 314 (17) 285 (6, M^+ – 2Me) 284 (2) 212 (4, $M^+ - C_8H_9$), 211 (3), 210 (2) 195 (4, $M^+ - OC_8H_9$) 194 (7, $M^+ - OC_8H_9$) 193 (2) 121 (17, OC_8H_9), 105 (13, C_8H_9).

Preparation of (2,6-Dimethylphenolato)titanatrane (18). The procedure was the same as for **16** except that 46.0 mg (0.38 mmol) of 2,6-dimethylphenol was used. Yield: 93%; mp, 181–183 °C; ^1H NMR ($CDCl_3$) δ 2.33 (s, 6 H, CH_3) 3.26 (t, 6H, $^3J_{H-H}$ = 5.7 Hz, NCH_2) 4.51 (t, 6H, $^3J_{H-H}$ = 5.7 Hz, OCH_2) 6.62 (t, 1H, $^3J_{H-H}$ = 7.5 Hz, *p*-H) 6.87 (d, 2H, $^3J_{H-H}$ = 7.5 Hz, *o*-H); ^{13}C NMR ($CDCl_3$) δ 17.07 (CH_3) 66.86 (NCH_2) 71.24 (OCH_2) 119.99, 127.54 (C_6H_3); MS, *m/e* (relative intensity) 316 (22, M^+) 315 (100, M^+) 314 (17) 286 (6, M^+ – 2Me) 285 (30, M^+ – 2Me) 284 (5) 211 (4, $M^+ - C_8H_9$) 210 (2, M^+, C_8H_9) 195 (4, $M^+ - OC_8H_9$) 194 (11, $M^+ - OC_8H_9$) 121 (6, OC_8H_9) 105 (10, C_8H_9).

Preparation of (2,4-Dimethylthiophenolato)titanatrane (19). The procedure was the same as for **16** except that 56.8 μL (58.0 mg, 0.38 mmol) of 2,4-dimethylthiophenol was used. Yield, 82% of red crystals; mp, 135–137 °C (dec); ^1H NMR ($CDCl_3$) δ 2.26 (s, 6 H, CH_3) 2.30 (s, 6 H, CH_3) 2.91 (t, 4 H, $^3J_{H-H}$ = 5.4 Hz, NCH_2) 3.10–3.19 (m, 4 H, NCH_2) 3.42–3.50 (m, 4 H, NCH_2) 4.60–4.86 (m, 12 H, OCH_2) 7.09 (d, 2 H, $^3J_{H-H}$ = 7.8 Hz, C_6H_3) 7.19 (s, 2 H, C_6H_3) 7.70 (d, 2 H, $^3J_{H-H}$ = 7.8 Hz, C_6H_3); ^{13}C NMR ($CDCl_3$) δ 20.78 (CH_3) 21.92 (CH_3) 57.42 (NCH_2) 60.79 (2 C, NCH_2) 73.11 (OCH_2) 77.73 (2 C, OCH_2), 126.26, 127.26, 129.76, 131.16, 131.18, 132.36 (C_6H_3); MS *m/e* (relative intensity) 332 (1, M^+) 227 (3, $M^+ - C_8H_9$) 194 (2, $M^+ - SC_8H_9$) 137 (40, SC_8H_9) 105 (30, C_8H_9).

Preparation of (2,6-Dimethylthiophenolato)titanatrane (20). The procedure was the same as for **16** except 0.16 g (0.60 mmol) of **14** and 0.08 mL (0.60 mmol) of 2,6-dimethylthiophenol was used. Yield, 68%; mp, 135–137 °C (dec); ^1H NMR ($CDCl_3$) δ, 2.42 (s, 12 H, CH_3), 2.84–3.45 (m, 12 H, NCH_2) 4.38–4.69 (m, 12 H, OCH_2) 6.87 (t, 2 H, $^3J_{H-H}$ = 8.1 Hz, *p*-H, 6.96 (d, 4 H, $^3J_{H-H}$ = 8.1 Hz, *m*-H); ^{13}C NMR ($CDCl_3$) δ 21.45 (CH_3) 58.42 (NCH_2) 62.44 (2 C, NCH_2) 74.03 (OCH_2) 77.20 (2 C, OCH_2) 126.66, 127.99, 128.02, 129.27 (C_6H_3); MS *m/e* (relative intensity) 332 (1, M^+) 331 (3, M^+) 227 (1, $M^+ - C_8H_9$) 194 (22, $M^+ - SC_8H_9$) 137 (22, SC_8H_9), 107 (57, C_8H_9).

Preparation of Titanatranylpinacolate (21). The procedure is the same as for **22** (see below) except that 0.55 g (2.1 mmol) of **14** was used. Mp., 232–234 °C; yield, 63%; ^1H NMR ($CDCl_3$) δ 1.20 (s, 6 H, $OC(CH_3)_2$) 1.29 (s, 6 H, $OCMe_2$) 3.14 (t, 6 H, $^3J_{H-H}$ = 7.2 Hz, NCH_2) 4.40 (t, 6 H, $^3J_{H-H}$ = 7.2 Hz, OCH_2); ^{13}C NMR ($CDCl_3$) δ 25.21 ($OC(CH_3)_2$) 25.64 ($OC(CH_3)_2$) 56.53 (NCH_2) 68.00 ($OCMe_2$) 70.40 (OCH_2) 72.58 ($OCMe_2$); MS *m/e* (relative intensity, 311 (1, M^+) 294 (3, M^+ – OH) 252 (48, $M^+ - CMe_2OH$) 194 (100, $M^+ - OC(Me)_2C(Me)_2OH$).

Preparation of Bis(titanatranyl)pinacolate (22). Compound **14** (1.1 g, 4.2 mmol) was reacted with pinacol (0.25 g, 2.1 mmol) in 30 mL of dry CH_2Cl_2. After stirring for 1.5 h at room temperature, the volume of the solution was reduced to about half under vacuum. This solution was carefully layered with about 40 mL of pentane and cooled to −25 °C. After 24 h, white crystals (0.9 g, 85% yield) of product appeared. The mother liquor from these crystals was kept at this temperature for 2 weeks during which time several crystals of X-ray quality appeared. Melting point, 202–204 °C (dec); ^1H NMR ($CDCl_3$) δ 1.35 (s, 12 H, $C(CH_3)_2$) 3.17 (t, 6 H, $^3J_{H-H}$ = 5.7 Hz, NCH_2) 4.51 (t, 6 H, $^3J_{H-H}$ = 5.7 Hz, OCH_2); ^{13}C NMR ($CDCl_3$) δ 24.92 ($C(CH_3)_2$) 61.15 (CH_2N) 72.53 (CH_2O) 76.49 ($OCMe_2$); MS, *m/e* (relative intensity) 504 (0.1, M^+) 252 (60.3, $^1/_2M^+$) 194 (100, $^1/_2M^+ - OCMe_2$) 164 (82, $^1/_2M^+ - OCMe_2 - OCH_2$). Anal. Calcd for $C_{18}H_{36}N_2O_8Ti_2$: C, 42.88; H, 7.20; N, 5.55. Found: C, 42.53; H, 7.37; N, 5.47.

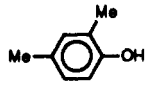
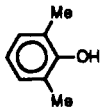
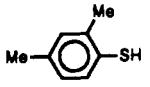
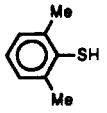
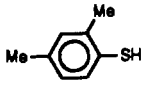
Preparation of 2-(Titanatranyloxy)-2,6-dimethyl-6-hydroxyhexane (23). The procedure was the same as for **22** except that **14** (0.30 g, 1.1 mmol) was reacted with 2,5-dimethyl-2,5-hexanediol (0.18 g, 1.23 mmol). (Yield, 92%; mp, 224–226 °C (dec); ^1H NMR ($CDCl_3$) δ 1.14 (s, 6 H, $C(CH_3)_2$) 1.29 (s, 6 H, $C(CH_3)_2$) 1.80 (s, 4 H, CH_2) 3.13 (t, 6 H, $^3J_{H-H}$ = 5.7 Hz, NCH_2) 4.38 (t, 6 H, $^3J_{H-H}$ = 5.7 Hz, OCH_2); ^{13}C NMR ($CDCl_3$) δ 29.29 ($OC(CH_3)_2$) 29.99 ($OC(CH_3)_2$) 37.55 ($Me_2(CH_2)$ 37.93 ($Me_2(CH_2)$ 55.74 (NCH_2) 69.99 (OCH_2) 70.60 (CMe_2); MS *m/e* (relative intensity) 340 (10) 339 (26, M^+) 338 (18).

Preparation of 2,6-Bis(titanatranyloxy)-2,6-dimethylhexane (24). The procedure is identical with that of **22** except that 0.55 g (2.10 mmol) of **14** was reacted with 0.16 g (1.10 mmol) of 2,5-dimethyl-2,5-hexanediol. Yield, 83%; mp, 208 °C (dec); ^1H NMR ($CDCl_3$) δ 1.32 (s, 12 H, $C(CH_3)_2$) 1.79 (s, 4 H, CH_2) 3.11 (t, 12 H, $^3J_{H-H}$ = 5.7 Hz, NCH_2) 4.38 (t, 12 H, $^3J_{H-H}$ = 5.7 Hz, OCH_2); ^{13}C NMR ($CDCl_3$) δ 29.35 $C(CH_3)_2$) 39.06 (CH_2) 55.65 (CH_2N) 70.04 (CH_2O) 81.63 ($OCMe_2$); MS, *m/e* (relative intensity) 532 (1, M^+) 504 (100, $M^+ - (CH_2CH_2)$) 502 (22, M^+ – 2Me), 338 (3, M – titanatranyl) 210 (15, titanatranyloxy).

Reactions of 14 with –OH and –SH Compounds. Stoichiometric amounts of the appropriate alcohol, silanol or thiol were added to **14** (30.0 mg, 0.11 mmol) dissolved in $CDCl_3$ in an NMR tube. After shaking for 1 min, the product was characterized by ^1H and ^{13}C NMR. In all four cases the NMR spectra were identical with the expected product (**3**,[1] **5**,[1] **9**,[2] and **11**[2]) plus free diethylamine.

Competitive Reaction of $Ti(NMe_2)_4$ and $Ti(NEt_2)_4$ with *tert*-Butyl Alcohol. In an NMR tube was dissolved 22.3 mg (0.10 mmol) of $Ti(NMe_2)_4$ and 33.6 mg (0.10 mmol) of $Ti(NEt_2)_4$ in C_6D_6. To this mixture was added 7.4 mg (9.4 μL, 0.1 mmol) of *tert*-butyl alcohol. The NMR tube was shaken for ~5 min and then the products were characterized by ^1H and ^{13}C NMR spectroscopy (see Discussion).

Table I. Pairwise Competition of **4**, **14**, and **15** in Reactions with –OH and –SH Compounds

reagent	% of **4** consumed	% of **14** consumed	% **15** consumed
Without $P(MeNCH_2CH_2)_3N$ Present			
PhOH	9	91	
	4	96	
	8	92	
t-BuOH	50	50	
EtOH	2	98	
Ph_3SiOH	10	90	
		96	4
	61		39
PhSH	15	85	
	14	86	
		90	10
	58		42
	11	89	
H_2O	5	95	
With $P(MeNCH_2CH_2)_3N$ Present			
Ph_3SiOH	44	56	
		97	3
	71		29
	46	54	
		93	7
	65		35

Competitive Reactions of 4, 14 and 15 with –OH and –SH Compounds. Equimolar amounts of pairs of the title compounds dissolved in $CDCl_3$ were reacted in an NMR tube with an equimolar amount of a reagent (see Table I). Competition reactions with the title compounds were also run in CD_3CN by reacting them with an equimolar mixture of reagent and the strong base $P(MeNCH_2CH_2)_3N$[7] dissolved in CD_3CN (Table I). All the reactions were carried out at ambient probe temperature. The ratio of reactants remaining were determined by integration of the ^1H NMR proton signals of the CH_3 groups of the liberated HNR_2.

Competitive Reaction of 4 with *p*-ClC_6H_4OH and *p*-MeC_6H_4OH. In 0.4 mL of dry $CDCl_3$ in an NMR tube was dissolved 0.07 g (0.29 mmol) of **4**. To this solution was added a mixture of 0.032 g (0.29 mmol) of *p*-methylphenol and 0.038 g (0.29 mmol) of *p*-chlorophenol dissolved in 0.4 mL of $CDCl_3$. The NMR tube was shaken for 1 min and analysis of the ^1H and ^{13}C NMR spectra attempted (see Discussion). In separate NMR tube experiments, equimolar amounts of *p*-methyl- or *p*-chlorophenol were added to 0.1 g (0.4 mmol) of **4** dissolved in $CDCl_3$. After shaking the NMR tube for 1 min, the ^1H and ^{13}C NMR spectra were taken.

25: ^1H NMR ($CDCl_3$) δ 3.27 (b, 6 H, NCH_2), 4.61 (b, 6 H, OCH_2), 6.92 (d, 2H, $^3J_{HH}$ = 6 Hz, Ph), 7.08 (d, 2 H, $^3J_{HH}$ = 6 Hz, Ph); ^{13}C NMR ($CDCl_3$) δ 61.4 (NCH_2), 72.4 (OCH_2), 102.1, 102.2, 123.8, 128.5 (Ph).

26: ^1H NMR ($CDCl_3$) δ 2.24 (s, 3 H, CH_3), 3.27 (b, 6 H, NCH_2), 4.61 (b, 6 H, NCH_2), 6.94 (b, 4 H, Ph); ^{13}C NMR ($CDCl_3$), 20.5 (CH_3), 61.1 (NCH_2), 72.2 (OCH_2), 118.5, 128.2, 129.0 (Ph).

Isotope Effect Study. Two 25 mL round bottom flasks equipped with a side arm were each charged with 0.30 g (1.3 mmol) of **4** and to each of them was added 5 mL of dry CH_2Cl_2. The reaction flasks were cooled to –30 °C and then simultaneously was added an equimolar amount of *t*-BuOH to one of the flasks and an equimolar amount of *t*-BuOD to the other. The reaction times were measured by a stop watch. Completion of the reaction was marked by the color change from yellow to colorless. This procedure was repeated with **14**.

Reaction of 4 with HFB_4·OEt_2. An NMR tube was charged with 0.16 g (0.060 mmol) of **14** in 0.6 mL of dry CD_3CN. After warming to effect solution and then cooling to room temperature, HBF_4·OEt_2 (0.01 g, 0.06 mmol) was added and the reaction mixture shaken for 3 min whereupon the solution turned from yellow to colorless. ^1H NMR (CD_3CN) δ 3.35, 4.55 ($FTi(OCH_2CH_2)_3N$, 3.24 (q, OCH_2CH_3, $^3J_{HH}$ = 6.9 Hz), 1.11 (t, OCH_2CH_3, $^3J_{HH}$ = 6.4 Hz), 2.54 (q, NCH_2CH_3, $^3J_{HH}$ = 7.2 Hz), 1.01 (t, NCH_2CH_3, $^3J_{HH}$ = 7.2 Hz); ^{19}F NMR (CD_3CN) δ 13.30, 13.35 ($FTi(OCH_2CH_2)_3N$), 11.63 (4 lines, Et_2NH·BF_3, $^1J_{BF}$ = 18 Hz). The ^{19}F NMR spectral assignments for Et_2NH·BF_3 compare favorably to that reported for Me_2NH·BF_3 ($\delta^{19}F$ = 11.1 ppm, $^1J_{BF}$ = 16.6 Hz[8]).

Reactions of 14 with NH_4Cl. This reaction was done in $CDCl_3$ analogously to the previous one. The yellow color of the starting material **14** was discharged immediately, giving proton NMR peaks characteristic of $HNEt_2$ (1.06 ppm, t, CH_2, $^3J_{HH}$ = 6.9 Hz; 2.59 ppm, q, CH_3, $^3J_{HH}$ = 6.9 Hz; 1.93 ppm, s, $HNEt_2/H_3N$) and chlorotitanatrane **13**[1] (3.28, 4.48, br, CH_2CH_2).

Competition Reaction of 4 with CF_3CH_2OH and EtOH. This was done analogously to the previous procedure except that the NMR spectra were obtained at –20 °C because of exchange of CF_3CH_2OH with $CF_3CH_2OTi(OCH_2CH_2)_3N$ noted at room temperature. The ratio of the reacted and unreacted CF_3CH_2OH was determined from the corresponding ratio of the ^{19}F NMR peaks that were well resolved at the lower temperature (see Discussion). In separate NMR tube experiments, an equimolar amount of CF_3CH_2OH ($\delta^{19}F$ = 84.4, –20 °C) was added to 0.1 (0.4 mmol) of **4** dissolved in $CDCl_3$. After shaking the NMR tube for 1 min, the ^{19}F NMR spectrum was taken. ^{19}F NMR ($CDCl_3$): δ 86.0 (20 °C), 85.9, 86.5 (1:1, –20 °C), 85.4, 85.7, 86.2 (1:3:2, –40 °C).

Competition Reaction of 4 with *i*-PrOH and Phenol. This was done analogously to the competition reaction of **4** with *p*-ClC_6H_4OH and *p*-MeC_6H_4OH except that the ratio of reacted and unreacted *i*-PrOH was determined by integration of the Me protons in the ^1H spectrum at –40 °C. At room temperature *i*-PrOH exchanged with **2**, giving only one doublet for these protons.

Single-Crystal X-ray Structures of 9 and 22. A solution of 0.5 g of **9** in 15 mL of dry CH_2Cl_2 was carefully layered with 50 mL of pentane.

Table II. Crystallographic Data for **9** and **22**

	9	**22**
formula	$C_{18}H_{38}N_2O_6S_2Ti_2$	$C_{18}H_{36}N_2O_8Ti_2$
fw	538.43	504.29
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a, Å	7.434(5)	6.6590(6)
b, Å	12.540(3)	17.819(2)
c, Å	7.034(3)	10.095(1)
α, deg	105.72(3)	
β, deg	98.87(3)	107.975(9)
γ, deg	85.30(4)	
V, Å^3	623.1(5)	1139.4(2)
Z	1	2
μ(Mo Kα), cm^{-1}	8.28	7.4
data collec instrument	Rigaku AFC6R	Rigaku AFC6R
temp, °C	–25	23
data		
R^a	0.043	0.044
$R_w{}^b$	0.061	0.054

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

Table III. Positional Parameters and *B*(eq) Values for **9**

atom	*x*	*y*	*z*	*B*(eq)
Ti	0.00104(6)	0.12576(4)	–0.02574(7)	1.70(2)
S	0.2071(1)	0.27177(6)	0.0662(1)	2.62(3)
O1	0.0705(3)	0.1024(2)	–0.2750(3)	2.46(8)
O2	–0.1445(3)	0.2082(2)	0.1562(3)	2.29(7)
O3	–0.1468(3)	–0.0204(2)	–0.0977(3)	2.29(7)
N	–0.2596(3)	0.1652(2)	–0.2133(3)	2.23(9)
C1	0.1753(4)	0.3667(3)	0.3094(5)	3.0(1)
C2	0.3222(6)	0.3502(4)	0.4717(6)	4.5(2)
C3	0.1680(8)	0.4855(3)	0.2929(7)	5.6(2)
C4	–0.2824(4)	0.2857(3)	0.1163(5)	3.2(1)
C5	–0.3133(5)	0.2778(3)	–0.1038(5)	3.4(1)
C6	–0.2232(5)	0.1548(4)	–0.4171(5)	4.2(2)
C7	–0.0185(5)	0.1611(3)	–0.4108(5)	3.3(1)
C8	–0.3994(5)	0.0872(3)	–0.2074(5)	3.3(1)
C9	–0.3154(4)	–0.0248(3)	–0.2254(5)	3.0(1)

(7) Laramay, M. A. H.; Verkade, J. G. *J. Am. Chem. Soc.* **1990**, *112*, 9421.

(8) Greenwood, N. N.; Hooten, R. A.; Walker, J. *J. Chem. Soc. (A)* **1966**, 21.

Table IV. Important Bond Distances (Å) and Angles (deg) for **9** and **22**

Bond Lengths for **9**

Ti1–S1 = 2.373(1)	Ti1′–O3 = 1.941(2)[a]
Ti1–O1 = 1.845(2)	Ti1–N1 = 2.269(3)
Ti1–O2 = 1.845(2)	Ti1–Ti1′ = 3.273(1)
Ti1–O3 = 2.117(2)	

Bond Angles for **9**

S1–Ti1–O3 = 171.03(6)	O3–Ti1–O3′ = 72.60(9)
O1–Ti1–O2 = 146.5(1)	Ti1–O3–Ti1′ = 107.40(9)
N1–Ti1–O3′ = 148.44(9)	

Bond Lengths for **22**

Ti1–O1 = 1.830(3)	Ti1–O4 = 1.776(2)
Ti1–O2 = 1.836(3)	Ti1–N1 = 2.282(3)
Ti1–O3 = 1.841(3)	

Bond Angles for **22**

O1–Ti1–O2 = 115.1(1)	O1–Ti1–N1 = 77.9(1)
O1–Ti1–O3 = 115.1(1)	Ti1–O4–C7 = 159.5(2)
O1–Ti1–O4 = 102.7(1)	O4–Ti1–N1 = 178.9(1)

[a] Ti1′ is the metal atom related to Ti1 by the inversion center.

Table V. Positional Parameters and B(eq) Values for **22**

atom	x	y	z	B(eq)
Ti	0.4679(1)	0.12186(3)	0.72354(6)	2.07(2)
O1	0.7477(4)	0.1173(2)	0.7360(3)	3.8(1)
O2	0.2943(4)	0.0601(1)	0.5917(3)	3.5(1)
O3	0.3677(4)	0.2166(1)	0.7399(3)	3.4(1)
O4	0.4624(4)	0.0778(1)	0.8802(2)	3.0(1)
N	0.4703(5)	0.1770(2)	0.5200(3)	3.0(1)
C1	0.8351(7)	0.1480(4)	0.6378(6)	5.1(2)
C2	0.6657(9)	0.1524(4)	0.4961(6)	6.0(3)
C3	0.2463(9)	0.0683(3)	0.4471(4)	4.4(2)
C4	0.2779(9)	0.1481(3)	0.4128(4)	4.8(2)
C5	0.3250(8)	0.2713(2)	0.6349(5)	4.1(2)
C6	0.457(1)	0.2572(3)	0.5409(5)	5.4(2)
C7	0.4046(5)	0.0267(2)	0.9703(3)	2.2(1)
C8	0.3582(8)	0.0726(3)	1.0845(5)	3.8(2)
C9	0.2069(7)	−0.0148(3)	0.8889(5)	3.7(2)

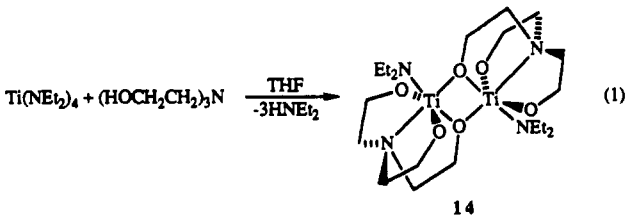
Over a period of 3 weeks at room temperature, large yellow crystals suitable for X-ray studies were grown. A yellow rectangular crystal of **9** and a colorless cube of **22** were mounted in glass capillaries inside an argon-filled glovebag. All measurements were made on a Rigaku AFC6R diffractometer with graphite monochromated Mo Kα radiation and a 12-kW rotating anode generator. Pertinent data collection and reduction information are given in Table II. Positional parameters and their estimated standard deviations and important bond distances and angles for **9** are collected in Tables III and IV. These data are given in Tables V and IV, respectively for **22**. The structure of **9** was solved by Patterson methods while that of **22** was solved by direct methods.[9,10] The non-hydrogen atoms of both structures were refined anisotropically. All hydrogen atoms in the latter structure were found from difference electron density maps. For structure **9** the hydrogen atom positions were calculated while for **22** the positional and isotropic thermal parameters were refined. All calculations were performed using the TEXSAN[11a] and the CHES[12] crystallographic software packages.

Neutral-atom scattering factors were taken from Cromer and Waber.[13] Anomalous dispersion effects were included in F_{calc};[14] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[11b]

(9) Beurskens, P. T. DIRDIF: Direct methods for difference structures-an automatic procedure for phase extension and refinement of difference structure factors. Technical Report 1984, Crystallography Laboratory, Toornooiveld, 6525 Ed. Nijmegen, Netherlands.
(10) Gilmor, C. J. Mithril. *J. Appl. Crystallogr.* **1984**, *17*, 42.
(11) (a) TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corp., 1985. (b) Cromer, D. T. *International Tables for X-ray Crystallography; The Kynoch Press: Birmingham, England, 1974; Table 2.3.1, Vol. IV.*
(12) Powell, D. R.; Jacobson, R. A. FOUR: A Generalized Crystallographic Fourier Program. U.S. DOE Report IS-4737, Iowa State University, Ames, IA, 1980.
(13) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974, Table 2.2A, Vol. IV.

Discussion

Synthesis of New Titanatranes. (Diethylamino)titanatrane (**14**) was synthesized in 82% yield according to reaction 1. The

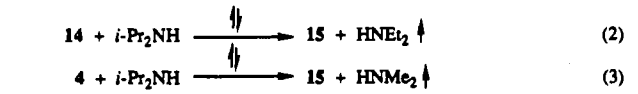


(1)

14

moisture-sensitive yellow crystalline material exhibits ^{1}H and ^{13}C NMR spectra from −45 to +45 °C similar to those of the dimethylamino derivative **4**.[2] We therefore believe **14** possesses the dimeric structure shown which is analogous to that determined for **4** by X-ray crystallography.[2] Attempts to synthesize **14** by reacting **4** with Et_2NH at room temperature in $CHCl_3$ or in refluxing toluene were not very successful. In the former case no reaction occurred and in the latter the residue which remained after evaporation was a complicated mixture which provided less than a 10% yield of **14** after several recrystallizations from CH_2Cl_2/pentane.

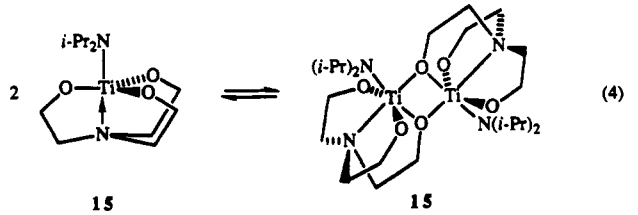
(Diisopropylamino)titanatrane **15** can be formed in quantitative and 85% yield via reactions 2 and 3, respectively, in which the



(2)

(3)

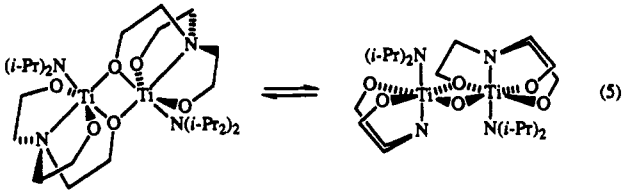
reagent titanatranes are refluxed in excess i-Pr_2NH. After work-up and recrystallization from CH_2Cl_2/pentane, however, the yield from reaction 2 was 61%. Refluxing **14** with a 50% molar excess of i-Pr_2NH in THF resulted in only a 24% conversion of **14** to **15**. The ^{1}H and ^{13}C NMR spectra of **15** could be taken to suggest the existence of equilibrium 4. The two broad peaks for the



(4)

15 **15**

CH_2CH_2 protons at room temperature for **15** progressively sharpen up to 45 °C. However, this observation is also consistent with a fluxional dimer as was suggested by us earlier for the similar behavior of **6**, for example.[1] Evidence for the dominance of equilibrium 5 is the lack of change in the breadth of the ^{1}H NMR



(5)

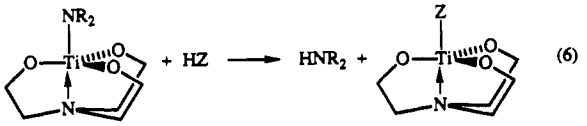
peaks upon dilution. If the dimeric configuration shown for **15** is correct, averaging of the CH_2CH_2 proton signals at elevated temperatures could occur via equilibrium 5 in which the configuration on the right permits intramolecular "gearing" around the N–Ti–N axes.[1] An attempt to react stoichiometric quantities of **14** with $HNPh_2$ at room temperature resulted in consumption of about half of compound **14** and the formation of several products according to ^{1}H NMR spectroscopy.

(14) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

Stirring a CH_2Cl_2 solution of **14** and the appropriate –OH or –SH compound at room temperature leads to **16–24** in isolated yields ranging from 82–93%, except for **20** and **21** which were isolated in 68 and 63% yields, respectively. Compounds **16–18** possess ^1H and ^{13}C NMR spectra consistent with monomeric and/or fluxionally dimeric behavior at room temperature. Unless an unobvious electronic effect is at play here, however, the considerable bulkiness of the aryl moieties in these compounds would seem more likely to induce a monomer/dimer equilibrium of type 4. By contrast, bulking the phenyl group of **11** with methyl groups in **19** and **20** does not appreciably change the ^1H and ^{13}C NMR spectral appearances from those of **11** which are consistent with dimeric behavior.[2] Thus the large size of the sulfur atom mitigates the bulk effect of the aryl groups in **19** and **20**. In the last section we show that the solid-state configuration of the (alkylthio)titanatrane **9** is indeed dimeric.

The facile syntheses of **21–24** from the appropriate diols and **14** is easily accomplished by controlling the stoichiometries. Heating a sample of **21** under vacuum at 90 °C for 48 h results in an 85% conversion to **22**. Compounds **21–24** exhibit ^1H and ^{13}C NMR spectra that are consistent with monomeric behavior, as might be expected from the presence of the bulky alkoxy substituents. Similar behavior was noted for the analogous *t*-BuO and Ph_3SiO derivatives **3** and **5**, respectively, of which **5** was shown by us earlier to be monomeric in the solid state.[1]

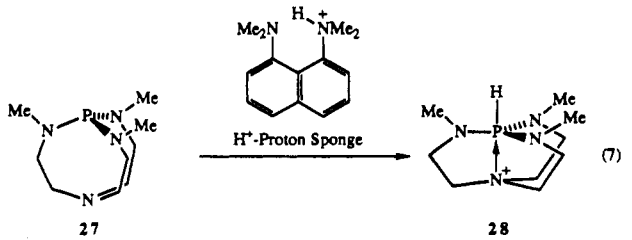
Comparative Reactivities of 4, 14, and 15. From Table I it is seen that in the absence of the base $P(MeNCH_2CH_2)_3N$, the relative rates of the reactions of the title compounds with labile hydrogen functional groups (reaction 6) are in the order **14** >>



(6)

4 R = Me
14 R = Et
15 R = *i*-Pr

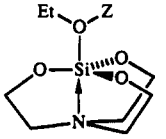
4 > **15**, indicating that the ease of displacement of the axial groups is in the order Et_2N >> Me_2N > $(i\text{-}Pr)_2N$. Here the order Et_2N >> Me_2N is counter to that expected on steric grounds. Interestingly, the basicities of the corresponding dialkyl amines in aqueous solution is $Et_2NH \cong (i\text{-}Pr)_2NH > Me_2NH$.[15] The basicity of the substituent nitrogen in **4**, **14** and **15** is likely to be enhanced by the transannular bond. Thus **27** quantitatively



(7)

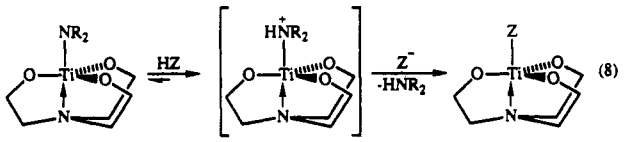
27 **28**

deprotonates strong protonated amine bases such as "Proton Sponge" to give cation **28** which has a pK_a of about 27 in DMSO.[5,7,16] This lone pair donation effect from the bridgehead nitrogen extends to the axial substituent atom in **29** which readily forms **30** and **31**, structures of which we have determined by X-ray means.[17]



	Z
29	nothing
30	···HOC(O)CF_3
31	—Me^+

To the extent that the aqueous basicity order $Et_2NH \cong (i\text{-}Pr)_2NH > Me_2NH$[15] can be assumed to hold for the R_2N substituents in **4**, **14** and **15**, a rather unconventional possibility for rationalizing the reactivity order Et_2N >> Me_2N > $(i\text{-}Pr)_2N$ is raised. The lower reactivity of **4** relative to **14** may be due to a lower concentration of the protonated species **32** than **33** in reaction 8 owing to the lower basicity of the Me_2N group compared



(8)

4 R = Me
14 R = Et
15 R = *i*-Pr

32
33
34

with Et_2N. If protonation occurs first, it would be expected to be very rapid compared with subsequent nucleophilic attack by Z^- on the titanium. Consistent with this supposition is the lack of a substantial isotope effect (1.1 at –30 °C) in the reaction of **4** with *t*-BuOH versus *t*-BuOD. The ratio was 1.25 in the analogous reaction of **14**. If it is indeed the concentration of a protonated intermediate such as **32** that dominates the rate of formation of product, then two HZ molecules of comparable steric size but contrasting acidities could be expected to display different reaction rates, with the more acidic HZ reactant reacting faster. The competition reaction of **4** with *p*-ClC_6H_4OH with *p*-MeC_6H_4OH proved inconclusive because of poorly resolved proton and ^{13}C NMR peaks in the reactant and corresponding product even for the CH_3 group. However, the competition reaction of **4** with CF_3CH_2OH and CH_3CH_2OH showed a rate ratio of 2.7 by ^{19}F NMR spectroscopy, and a similar competition reaction involving PhOH and *i*-PrOH revealed a rate ratio of 3.9 by ^1H NMR spectroscopy of the *i*-Pr methyl protons. The latter result also favors intermediate **32** because RO^- is more nucleophilic than ArO^-.

The rate of nucleophilic attack by Z^- compared with the protonation step in reaction 8, is expected to be much slower. Since the steric A factor for an Et group (1.75 kcal/mol[18]) is close to that of Me (1.70 kcal/mol[18]), the higher concentration of **33** may be expected to dominate the substitution rate by Z^-. Since Et_2NH and $(i\text{-}Pr)_2NH$ have similar basicities,[15] the much slower departure of the $HN^+(i\text{-}Pr)_2$ moiety in **34** is attributable to its steric inhibiting effect on the Ti center to nucleophilic attack, since the *A* factor for the *i*-Pr group is 2.15 kcal/mol.[18] Such a steric argument is also consistent with the low rate of substitution of **15** relative to **4**, despite the greater basicity of the $(i\text{-}Pr)_2N$ group in the former.

The approximately equal reactivities of **4** and **14** to *t*-BuOH may be ascribed to the bulky nature of *t*-BuOH coupled with its relatively low acidity (compared with $HOSiPh_3$, for example, with which **14** is much more reactive than **4**). Thus the reactions of **14** and **4** may proceed predominantly by nucleophilic attack of undissociated *t*-BuOH (which would be expected to be controlled by steric factors) and partially by protonation which would be preferential in the case of **14**. This conclusion is consistent with the results of the isotope effect studies utilizing *t*-BuOH and *t*-BuOD (see above).

Substantiation of an intermediate such as **32** could be provided by reacting **4** with protonic acid with a nonnucleophilic anion. In

(15) The pK_a values for $HNEt_2$ (11.090) and $HN(i\text{-}Pr)_2$ (11.13) are within experimental error, while the value for $HNMe_2$ is 10.992 (Perrin, D. D. *Dissociation Constants of Organic Bases in Aqueous Solution, Supplement*; Butterworths: London, 1972).

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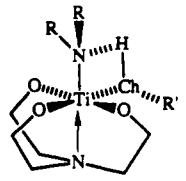
(17) Garant, R. J.; Daniels, L. M.; Das, S. K.; Janakiraman, M. N.; Jacobson, R. A.; Verkade, J. G. *J. Am. Chem. Soc.* **1991**, *113*, 5728.

(18) The conformational free energy difference between axial and equatorial conformations of monosubstituted cyclohexanes (Hirsch, J. A. *Top. Stereochem.* **1967**, *1*, 199).

NMR tube experiments in CD_3CN, $HBF_4{\cdot}OEt_2$ reacted immediately with **14** to give fluorotitanatrane, $Et_2NH{\cdot}BF_3$ and Et_2O. By contrast, $NaBF_4$ does not react with **4**. Thus the normally nonnucleophilic BF_4^- ion here is slightly dissociated in CD_3CN to BF_3 and F^- (as is substantiated by its broad ^{19}F NMR resonance—see Experimental Section). However, the F^- is apparently not able to displace the R_2N group without the assistance of a H^+. This was also shown to be the case in the similarly contrasting results of **14** in the presence of NH_4Cl and Me_4NCl. In the former case, the NEt_2 group of **14** was immediately displaced to give chlorotitanatrane **13**, whereas no reaction was observed to occur with Me_4NCl. This suggests that the NH_4^+ protonates the strongly basic NEt_2 group of **14**, thus assisting the latter's departure as $HNEt_2$ in the presence of the nucleophilic chloride ion.

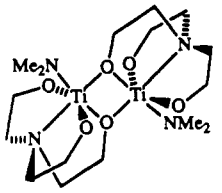
In the presence of the exceedingly strong base $P(MeNCH_2CH_2)_3N$,[7] the order of axial group substitution is **14** ≥ **4** > **15**. The approximately equal rates for **14** and **4** suggest predominance of attack by Z^-, with greatly reduced concentrations of species **32** and **33**, respectively. The concentration of **33** may still be sufficient, however, to compete with **4**. The comparatively low reactivity of **15** compared with **14** and **4** is consistent with the relatively large size of the $N(i\text{-}Pr)_2$ group. Interestingly, the reactivity of **15** relative to **4** is further decreased when the base is present, suggesting that preferential protonation of the $(i\text{-}Pr)_2N$ group in **15** (giving **34**) plays an accelerating role in the absence of the base. The substantially constant relative reactivity of **14** and **15** in the absence or presence of base is consistent with the notion that the degree of protonation is about the same for both compounds in the absence of base (since the corresponding R_2N groups are closely equivalent in basicity) and that the relative reactivities are sterically controlled. While these experiments do not prove the dominance of a preprotonation step in the absence of base, they are consistent with such a hypothesis.

Another pathway to consider is that involving a hydrogen-bonded intermediate analogous to **30** followed by the formation of a four-center intermediate of type **35**. If RCh–H bond breakage



Ch = chalcogen

35



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in **35** were the rate-determining step, a substantial isotope effect should have been observed (see above). While evidence cited above is not consistent with initial attack of HChR on **4**, **14** and **15** as the rate-determining step (i.e., faster attack of PhOH on **4** than *i*-PrOH despite the nucleophilicty order $RO^- > ArO^-$), proton-assisted cleavage of the Ti–NR_2 bond in **35** is also a possibility. From a consideration of all the available evidence, however, we tend to favor preprotonation as the dominant path.

Intermediates such as **32–35** could arise from equilibrium dissociation of dimeric species, for which there is solid-state and solution evidence (see below). Indeed, protonated or four-center intermediates can even be envisioned to arise from a dimeric structure such as that found for **4**.[2] In such a structure, a four-center intermediate would confer seven-coordination on the Ti atom; a configuration we have observed in the solid state for **36** which contains a bidentate acetate group.[1] In any case, the arguments made here about the relative reactivities of **4**, **14** and **15** are not affected by their degrees of oligomerization, provided the plausible assumptions are made that oligomerizations are similar and that the rates of oligomer dissociation are similar. In this regard it should be noted that if intermediates **32–34** are dimeric, they may possess a structure analogous to **2** instead of

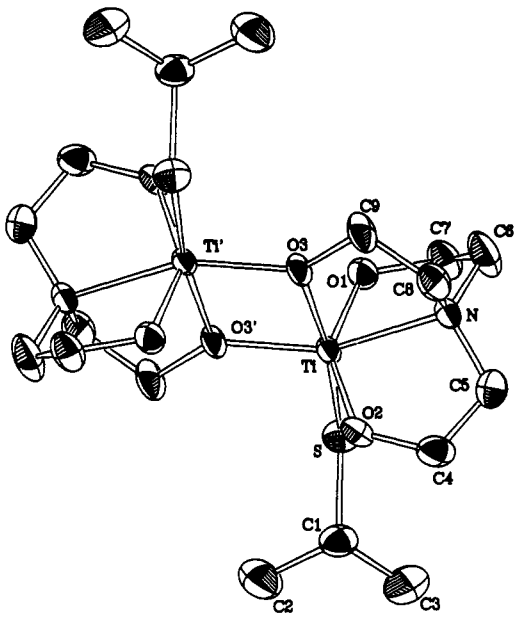
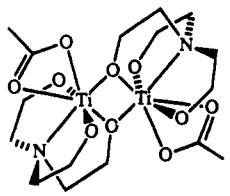
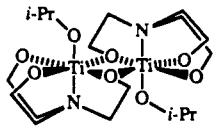


Figure 1. ORTEP drawing of **9**. The ellipsoids are drawn at the 50% probability level. Describing the coordination sphere about the Ti atom as a distorted trigonal pyramid, we consider atoms O3', O1 and O2 to define the equatorial plane with atoms O3 and S to lie above and below as the approximately axial positions.



36



2

4, since only highly electron inducting substituents such as R_2N[2] and RS (see later) prefer to be trans to a more electronegative atom such as oxygen instead of nitrogen. It may also be mentioned that the ^{19}F spectrum of $CF_3CH_2O\overline{Ti(OCH_2CH_2)_3N}$ at −20 °C displayed two peaks (85.9 and 86.5 ppm) in a 1:1 ratio. While this result suggests the presence of an oligomer(s), further work will have to be done to clarify its origin.

Three additional curious observations from the data in Table I can be made: (a) Increasing *ortho*-methyl substitution in the phenols and thiophenols does not appreciably influence the relative reactivities of **4** and **14**, (b) EtOH, though less acidic (pK_a = 16) than phenol (pK_a = 9.9) gives rise to about the same reactivity ratio as phenol with **4** and **14**. This can be attributed mainly to the greater nucleophilicity of RO^- over ArO^- and the size order $EtO^- < PhO^-$. In the case of H_2O, the proton concentration would be expected to lie between that of phenol and ethanol, and the nucleophilicity of OH^- also lies between that of RO^- and ArO^-. Thus, the opposing orders of proton concentration ($ROH < H_2O < PhOH$) and nucleophilicity ($RO^- > OH^- > PhO^-$) may be expected to compensate to provide roughly equal relative reactivities for **4** and **14**. (c) Last, the somewhat greater reactivity of the thiophenols than phenols toward **14** relative to **4** might be associated with the normally expected nucleophilicity order $ArS^- > ArO^-$. It is not clear, however, what to assume for the acidity order of ArSH and ArOH in $CDCl_3$ (the solvent used for our experiments) since the acidity order is reversed from solvents such DMF and DMSO (PhOH < PhSH[19]) to H_2O (PhSH > PhOH) owing to solvent effects.

Solid-State Structures of 9 and 22. Since the solid-state structures of **2**[20] and **4**[2] determined by X-ray means reveal different

(19) Maran, F.; Celadon, D.; Severin, M. G.; Vianello, E. *J. Am. Chem. Soc.* **1991**, *113*, 9320.

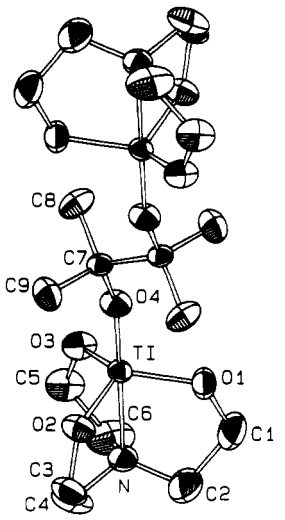
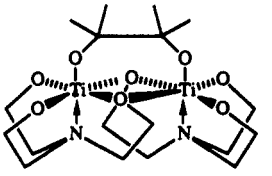


Figure 2. ORTEP drawing of **22**. The ellipsoids are drawn at the 50% probability level.

configurations, it was of interest to carry out a similar determination for **9**. The VT ^{1}H NMR behavior of **9** and **4**[2] are quite similar (suggesting relatively rigid dimeric behavior) whereas the behavior of **2** is consistent with a fluxional dimer.[1] As the ORTEP drawing of **9** in Figure 1 illustrates, the solid-state configurations of **9** and **4** are the same, featuring a trans relationship of the axial substituent with an oxygen in each case, rather than with the tertiary nitrogen as in **2**. Earlier we suggested that the more electron-donating Me_2N substituent in **4** prefers to be trans to an oxygen rather than to the more electron-donating nitrogen, thus rationalizing the configurational contrast with **2** in which a more electronegative alkoxy substituent is present.

The metal–metal distance (3.273(1) Å) in **9** is longer than in **4** (3.2547(6) Å and shorter than in **2** (3.356(1) Å), but too long for appreciable metal–metal interaction. The Ti–O (terminal) bond lengths in **9** (avg 1.845(2) Å) are somewhat shorter than in **4** (avg 1.877 (1) Å). The slightly shorter TiO3 distance in **9** (2.117(2) Å) compared with that in **4** (2.160(1) Å[2]) is attributable to the greater σ and/or π electron induction by the Me_2N substituent. The Ti–S bond length in **9** (2.373(1) Å) compares favorably with other such lengths reported.[21]

The ORTEP drawing of **22** in Figure 2 represents the first reported structure of two linked titanatranyl moieties. Our main purpose in determining the structure of this molecule was to ascertain whether the dimerization tendency of titanatranes was sufficiently strong to cause intramolecular ring formation depicted as



in which the molecular dipoles would be aligned rather than opposed as in **2**. The tertiary alkyls on the axial oxygens would presumably inhibit intermolecular association (with opposing dipolar arrangements) owing to their bulk, since we observed that **5** is monomeric in the solid state.[1] Although oligomer formation was prevented, ring formation did not occur. Except for the expected metric differences associated with the axial substituent in **2** and **22**, the bond lengths and angles are very comparable in the two structures.

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Supplementary Material Available: Tables of crystal data, bond distances, bond angles, hydrogen atom positional parameters, and general displacement parameter expressions (20 pages). Ordering information is given on any current masthead page.

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