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Article

Trisilane-1,3-diolato Complexes of Ti and Zr: Syntheses and X-ray Crystal Structures[†]

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The syntheses and structures of zirconium and titanium complexes containing the novel chelating trisilane-1,3-diolate ligand $[Me_2Si(R_2SiO)_2]^{2-}$ ($R = SiMe_3$) (**5**)-H_2 are reported. The chloride complexes $[Me_2Si(R_2SiO)_2]TiCl_2$ (**7a**) and $[Me_2Si(R_2SiO)_2]ZrCl_2 \cdot 2THF$ (**7b**) were prepared by the reaction of MCl_4 ($M = Ti$, Zr) with $[Me_2Si(R_2SiO)_2]_2Ti$ (**6a**) and $[Me_2Si(R_2SiO)_2]_2Zr$ (**6b**), which are derived from the reaction of **5** with $M(NEt_2)_4$, respectively. In the presence of $TiCl_4$, complexes **6a** and **7a** undergo a ring-opening reaction to produce the dinuclear complex $[Me_2Si(R_2SiO)_2][TiCl_3]_2$ (**9**). $[Me_2Si(R_2SiO)_2]TiMe_2$ (**10**) and $[Me_2Si(R_2SiO)_2]TiBnz_2$ (**11**) were prepared in moderate yields from reactions of **7a** with 2 equiv of MeMgBr and BnzMgCl, respectively. According to NMR spectroscopic investigations, the reaction of the dimethyltitanium complex **10** with $B(C_6F_5)_3$ led to full exchange of both methyl groups by C_6F_5 groups under quantitative formation of $[Me_2Si(R_2SiO)_2]Ti(C_6F_5)_2$ (**12**) and a mixture of $B(C_6F_5)_{3-n}Me_n$, where $n = 1$–3. The structure of **12** is further evidenced by the preparation of an identical sample from the reaction of **7a** with 2 equiv of C_6F_5MgBr. Refluxing an ether solution of **12** surprisingly gave $[Me_2Si(R_2SiO)_2]_2TiC_6F_5]_2O$ (**13**) as a result of ether cleavage. The structures of the complexes **7a**, **7b**, **9**, **10**, and **13** were determined by X-ray crystallography, and structural discussion of the bond parameters will be given.

Introduction

In addition to being precursors for metal oxides and silicates in sol−gel and related processes[1] and models for silica-supported heterogeneous catalysts,[2] group 4 metal silanolates[3] derived from silanediols, silanetriols, disiloxanediols, trisiloxanediols, and related species have found applications as catalysts in olefin polymerizations,[4] olefin metatheses,[5] C−H activation,[6] and oxidation reactions.[1h,7] Silanolate ligands similar to alkoxides are capable of being

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[†] Dedicated to Prof. M. H. Chisholm on the occasion of his 60th birthday.

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σ and π donors,[8] which, important for catalytic processes, enable electronic stabilization of oxophilic metal ions in relatively high oxidation states. For example, a dinuclear zirconium complex derived from the reaction of $Zr(Bnz)_4$ with $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$, an incompletely condensed polyhedral oligosilsesquioxane, provides after treatment with $B(C_6F_5)_3$ a highly active olefin polymerization catalyst system.[9]

In this context, cp-free mononuclear cyclic complexes of group 4 metals containing bidentate silanediolates of the general formula $[Y(R_2SiO)_2]^{2-}$, where Y = O, $(R_2SiO_2)_n$, $(R_2Si)_n$, or $(CH_2)_n$, might be interesting catalyst candidates because they may be considered as analogues to *ansa*-metallocenes[10] or cp-containing half-sandwich complexes of "constraint geometry",[11] which form highly active Ziegler–Natta catalysts with boranes or methylaluminoxane.

Particularly, the coordination chemistry of α,ω-siloxanediolates, $[O(Ph_2SiO)_n]^{2-}$ ($n = 1-3$), is well established and documented in a recent review paper by King and Sullivan,[3c] and a number of different neutral or negatively charged spirocyclic silanolate complexes have been reported.[12] However, constrained five- and six-membered monocyclic silanediolates of group 4 metals are rare. Apart from only a handful of titanium- and zirconium-containing five-membered ring compounds developed in our laboratory,[13] six-membered cyclic complexes, $[Y(R_2SiO)_2]MX_2$, where X is a reactive group such as halides amide, or alkyl are unknown in the literature.[14]

Therefore, our initial efforts have been directed toward developing new monocyclic complexes containing dianionic trisilane-1,3-diolates. Herein we describe the synthesis of the novel ligand $[Me_2Si(R_2SiO)_2]H_2$, and among others we report on the preparation and X-ray structures of a series of titanium and zirconium complexes of the general formula $[Me_2Si(R_2SiO)_2]MX_2$, where X = Cl, Me, Bnz, and C_6F_5.

Experimental Section

General Procedure. All manipulations of air- and/or moisture-sensitive compounds were carried out under an atmosphere of argon using standard Schlenk and glovebox techniques. Tetrahydrofuran (THF), diethyl ether, *n*-heptane, and *n*-pentane were distilled under argon from alkali metals prior to use. CH_2Cl_2 was distilled from CaH_2 and stored over molecular sieves. Benzene-d_6 was dried over activated molecular sieves and stored in the glovebox. The oligosilane **3**[16] and $B(C_6F_5)_3$[36] were prepared as previously described. NMR: Bruker AC 250, Bruker ARX 300, Bruker ARX 500. IR: Nicolet 205 FT-IR. MS: Intectra AMD 402, chemical ionization with isobutane as the reactant gas.

2,4-Dihydroxy-1,1,1,3,3,5,5,5-octamethyl-2,4-bis(trimethylsilyl)pentasilane (5). Freshly distilled trifluoromethanesulfonic acid (TfOH; 10.5 mL, 0.12 mol) was added at −40 °C to a stirred solution of **3** (31.4 g, 0.056 mol) in CH_2Cl_2 (250 mL), and the mixture was allowed to warm to room temperature within 2 h. After the solvent was changed from CH_2Cl_2 to diethyl ether, an aqueous solution of NH_4COONH_2 (120 mL, 1 M) was added, and stirring was continued for 30 min. The organic phase was separated and dried over $MgSO_4$, and the solvent was evaporated. Drying under vacuum afforded 24.3 g (98%) of the title compound, which was kept in a freezer. An analytically pure sample was obtained. Mp: 117–119 °C. ^1H NMR (C_6D_6, 250 MHz): δ 1.57 (s, br, OH, 2 H), 0.43 (s, $Si(CH_3)_2$, 6 H), 0.29 (s, $Si(CH_3)_3$, 36 H). ^{13}C NMR (C_6D_6, 62.9 MHz): δ −0.2 ($Si(CH_3)_3$), −1.5 ($Si(CH_3)_2$). ^{29}Si NMR INEPT (C_6D_6, 79.5 MHz): δ 7.5 (SiO), −15.3 ($Si(CH_3)_3$), −35.6 ($Si(CH_3)_2$). MS (70 eV): *m/z* (%) 439 (3) $[M^+]$, 422 (2) $[M^+ - OH]$, 367 (19) $[M^+ - Si(CH_3)_3]$ 349 (57) $[M^+ - OH - Si(CH_3)_3]$. Anal. Calcd for $C_{14}H_{44}O_2Si_7$ (441.10): C, 38.12; H, 10.05. Found: C, 37.01; H, 9.67.

$\{SiMe_2[(Me_3Si)_2SiO]_2\}_2Ti$ (6a). $Ti(NEt_2)_4$ (2.15 mL, 5.95 mmol) was added to a stirred solution of **5** (5 g, 11.34 mmol) in *n*-heptane (70 mL) at room temperature. The reaction mixture was refluxed for 2 h, and all volatiles were removed under vacuum. An analytically pure sample of **6a** was obtained by crystallization from *n*-pentane at 4 °C. Yield: 3.5 g (67%). Mp: >230 °C. ^1H NMR (C_6D_6, 250 MHz): δ 0.49 (s, $Si(CH_3)_2$, 12 H), 0.36 (s, $Si(CH_3)_3$, 72 H). ^{13}C NMR (C_6D_6, 62.9 MHz): δ −0.2 ($Si(CH_3)_3$), −1.5 ($Si(CH_3)_2$). ^{29}Si NMR INEPT (C_6D_6, 79.5 MHz): δ 11.7 (SiO), −14.4 ($Si(CH_3)_3$), −35.7 ($Si(CH_3)_2$). MS (70 eV): *m/z* (%) 926 (75) $[M^+]$, 911 (11) $[M^+ - CH_3]$, 853 (11) $[M^+ - Si(CH_3)_3]$. Anal. Calcd for $C_{28}H_{84}O_4Si_{14}Ti$ (926.08): C, 36.32; H, 9.14. Found: C, 36.05; H, 9.11.

$\{SiMe_2[(Me_3Si)_2SiO]_2\}TiCl_2$ (7a). Analogously to the procedure described above, raw **6a** derived from **5** (4 g) and $Ti(NEt_2)_4$ (1.72 mL, 4.76 mmol) was dissolved in *n*-pentane (50 mL) and cooled to −40 °C. After a 1 M solution of $TiCl_4$ (4.8 mL, 4.8 mmol) in toluene was added, the orange solution was stirred for 10 min and allowed to warm to room temperature. Crystallization of a concentrated *n*-pentane solution in a freezer affords the title compound as orange crystals. Total yield: 3.3 g (65%). Mp: 133 °C (dec). ^1H NMR (C_6D_6, 250 MHz): δ 0.43 (s, $Si(CH_3)_2$, 6 H), 0.25 (s, $Si(CH_3)_3$, 36 H). ^{13}C NMR (C_6D_6, 75.5 MHz): δ −0.3 ($Si(CH_3)_3$), −1.4 ($Si(CH_3)_2$). ^{29}Si NMR INEPT (C_6D_6, 59.6 MHz): δ 35.7 (SiO), −10.7 ($Si(CH_3)_3$), −34.2 ($Si(CH_3)_2$). MS (70 eV): *m/z* (%) 556 (12) $[M^+]$, 541 (3) $[M^+ - CH_3]$, 483 (2) $[M^+ - Si(CH_3)_3]$, 349 (47) $[M^+ - Si(CH_3)_3 - OTiCl_2]$. Anal. Calcd for $C_{14}H_{42}Cl_2O_2Si_7Ti$ (557.87): C, 30.14; H, 7.59; Cl, 12.71. Found: C, 29.37; H, 7.61; Cl, 12.40.

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$\{SiMe_2[(Me_3Si)_2SiO]_2\}TiCl_2\cdot TMEDA$ (8a). *N*,*N*-Tetramethylethylenediamine (TMEDA; 45.3 mg, 0.39 mmol) was added at 0 °C to a solution of **7a** (0.2 g, 0.36 mmol) in *n*-pentane, upon which an orange precipitate formed. After dissolution in the heat, orange crystals precipitated from the solution upon cooling to room temperature and were collected, washed with *n*-pentane, and dried under vacuum. Yield: 0.21 g (88%). Mp: 174 °C. ^{1}H NMR (C_6D_6, 250 MHz): δ 2.53 (s, NCH_3, 12 H), 1.95 (s, NCH_2, 4 H), 0.64 (s, $Si(CH_3)_2$, 6 H), 0.48 (s, $Si(CH_3)_3$, 36 H). ^{13}C NMR (C_6D_6, 75.5 MHz): δ 57.5 (NCH_2), 52.1 (NCH_3), 1.4 ($Si(CH_3)_3$), −0.8 ($Si(CH_3)_2$). ^{29}Si NMR INEPT (C_6D_6, 59.6 MHz): δ 18.9 (SiO), −11.6 ($Si(CH_3)_3$), −44.0 ($Si(CH_3)_2$). Anal. Calcd for $C_{20}H_{58}Cl_2O_2N_2Si_7Ti$ (674.06): C, 35.64; H, 8.67; N, 4.16. Found: C, 35.82; H, 8.65; N, 4.11.

$\{SiMe_2[(Me_3Si)_2SiO]_2\}_2Zr$ (6b). $Zr(NEt_2)_4$ (0.9 mL, 2.43 mmol) was added to a stirred solution of **5** (2 g, 4.53 mmol) in *n*-heptane (30 mL) at room temperature. The reaction mixture was refluxed for 2 h, and all volatiles were removed under vacuum to leave raw **6b** as a white solid nearly quantitatively. An analytically pure sample can be obtained by crystallization from *n*-pentane at 4 °C. Yield: 1.2 g (55%). Mp: 139 °C. ^{1}H NMR (C_6D_6, 250 MHz): δ 0.47 (s, $Si(CH_3)_2$, 12 H), 0.33 (s, $Si(CH_3)_3$, 72 H). ^{13}C NMR (C_6D_6, 62.9 MHz): δ −0.3 ($Si(CH_3)_3$), −1.1 ($Si(CH_3)_2$). ^{29}Si NMR INEPT (C_6D_6, 59.6 MHz): δ 3.4 (SiO), −14.3 ($Si(CH_3)_3$), −35.6 ($Si(CH_3)_2$). MS (70 eV): *m*/*z* (%) 968 (100) [M^+], 953 (12) [$M^+ - CH_3$], 895 (15) [$M^+ - Si(CH_3)_3$]. Anal. Calcd for $C_{28}H_{84}O_4Si_{14}Zr$ (969.39): C, 34.69; H, 8.73. Found: C, 33.88; H, 8.82.

$\{SiMe_2[(Me_3Si)_2SiO]_2\}ZrCl_2\cdot 2THF$ (7b). Raw **6b** derived from **5** (1.18 g, 2.68 mmol) and $Zr(NEt_2)_4$ (0.52 mL, 1.41 mmol) was dissolved in THF (30 mL), cooled to −78 °C, and added to freshly sublimed $ZrCl_4$ (0.38 g, 1.62 mmol). After stirring was continued for 4 h at room temperature, the solvent was removed under vacuum, the remaining solid was refluxed in *n*-heptane, and the hot suspension was filtered. After cooling to room temperature, colorless crystals of **7b** precipitated from the solution, which were collected, washed with *n*-pentane, and dried under vacuum. Total yield: 0.79 g (40%). Mp: 194 °C. ^{1}H NMR (C_6D_6, 250 MHz): δ 3.96 (m, OCH_2CH_2, 8 H), 1.33 (m, OCH_2CH_2, 8 H), 0.63 (s, $Si(CH_3)_2$, 6 H), 0.49 (s, $Si(CH_3)_3$, 36 H). ^{13}C NMR (C_6D_6, 62.9 MHz): δ 72.4 (OCH_2CH_2), 25.3 (OCH_2CH_2), 0.7 ($Si(CH_3)_3$), −0.8 ($Si(CH_3)_2$). ^{29}Si NMR INEPT (C_6D_6, 59.6 MHz): δ 1.8 (SiO), −13.2 ($Si(CH_3)_3$), −50.4 ($Si(CH_3)_2$). MS (70 eV): *m*/*z* (%) 600 (22) [M^+], 585 (9) [$M^+ - CH_3$], 527 (9) [$M^+ - Si(CH_3)_3$], 349 (88) [$M^+ - Si(CH_3)_3 - OZrCl_2$]. Anal. Calcd for $C_{14}Cl_2H_{42}O_2Si_7Zr\cdot 2THF$ (745.42): C, 35.45; H, 7.84; Cl, 9.51. Found: C, 34.75; H, 7.90; Cl, 9.47.

$\{SiMe_2[(Me_3Si)_2SiO]_2\}ZrCl_2\cdot TMEDA$ (8b). TMEDA (21.4 mg, 0.18 mmol) was added at 0 °C to a solution of **7b** (0.13 g, 0.17 mmol) in *n*-heptane, upon which a white precipitate formed. After redissolution in the heat, crystals precipitated from the solution upon cooling to room temperature, which were collected, washed with *n*-heptane, and dried under vacuum. Yield: 88 mg (73%). Mp: 181 °C (dec). ^{1}H NMR (C_6D_6, 250 MHz): δ 2.36 (s, NCH_3, 12 H), 1.81 (s, NCH_2, 4 H), 0.63 (s, $Si(CH_3)_2$, 6 H), 0.49 (s, $Si(CH_3)_3$, 36 H). ^{13}C NMR (C_6D_6, 75.5 MHz): δ 57.0 (NCH_2), 50.7 (NCH_3), 0.9 ($Si(CH_3)_3$), −0.6 ($Si(CH_3)_2$). ^{29}Si NMR INEPT (C_6D_6, 59.6 MHz): δ 3.0 (SiO), −13.0 ($Si(CH_3)_3$), −49.9 ($Si(CH_3)_2$). Anal. Calcd for $C_{20}H_{58}Cl_2O_2N_2Si_7Zr$ (717.42): C, 33.48; H, 8.15; N, 3.90. Found: C, 33.39; H, 8.12; N, 3.83.

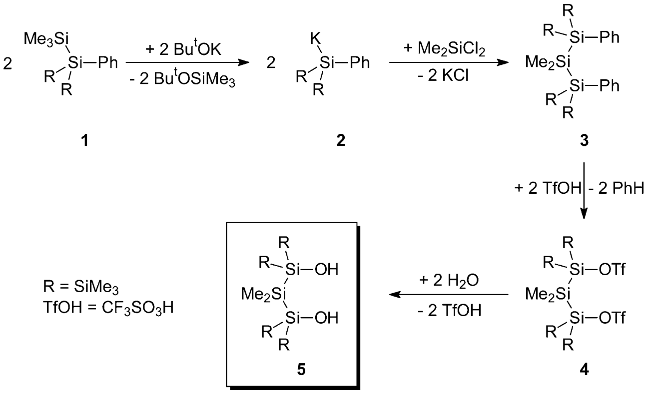
$\{SiMe_2[(Me_3Si)_2SiO]_2\}Ti_2Cl_6$ (9). A solution of $TiCl_4$ (1 M, 1.6 mL, 1.6 mmol) in toluene was added to **6a** (0.44 g, 0.475 mmol) at −40 °C. Crystallization from a concentrated *n*-pentane solution in a freezer afforded the title compound as red-orange crystals. Yield: 0.58 g (82%). Mp: 110 °C. ^{1}H NMR (C_6D_6, 250 MHz): δ 0.58 (s, $Si(CH_3)_2$, 6 H), 0.32 (s, $Si(CH_3)_3$, 36 H). ^{13}C NMR (C_6D_6, 75.5 MHz): δ 0.6 ($Si(CH_3)_3$), −2.0 ($Si(CH_3)_2$). ^{29}Si NMR INEPT (C_6D_6, 59.6 MHz): δ 69.1 (SiO), −8.6 ($Si(CH_3)_3$), −28.7 ($Si(CH_3)_2$). MS (70 eV): *m*/*z* (%) 558 (23) [$M^+ - TiCl_4$], 543 (6) [$M^+ - TiCl_4 - CH_3$], 350 (29) [$M^+ - TiCl_4 - OTiCl_2 - Si(CH_3)_3$], 188 (50) [$TiCl_4$]. Anal. Calcd for $C_{14}H_{42}Cl_6O_2Si_7Ti_2$ (747.53): C, 22.49; H, 5.66. Found: C, 22.41; H, 5.56.

$\{SiMe_2[(Me_3Si)_2SiO]_2\}TiMe_2$ (10). A 3 M solution of MeMgBr (1 mL, 3 mmol) in diethyl ether was added dropwise to a slurry of **7a** (0.75 g, 1.344 mmol) in ether (10 mL) at −78 °C. The heterogeneous mixture was stirred for 15 min and allowed to warm to room temperature within 30 min, after which time the solvent was removed under vacuum. The product was extracted with *n*-pentane and filtered, and the solution was concentrated. Crystallization at −40 °C afforded the title compound as highly air- and moisture-sensitive material. Because of a slow decomposition after several weeks at room temperature, **10** was kept in a freezer (−40 °C), where it is stable for months. Yield: 0.48 g (69%). Mp: 118 °C (dec). ^{1}H NMR (C_6D_6, 300 MHz): δ 0.88 (s, $Ti(CH_3)_2$, 6 H), 0.44 (s, $Si(CH_3)_2$, 6 H), 0.30 (s, $Si(CH_3)_3$, 36 H). ^{13}C NMR (C_6D_6, 75.5 MHz): δ 49.2 ($Ti(CH_3)_2$), −0.2 ($Si(CH_3)_3$), −0.7 ($Si(CH_3)_2$). ^{29}Si NMR INEPT (C_6D_6, 59.6 MHz): δ 14.7 (SiO), −13.5 ($Si(CH_3)_3$), −26.6 ($Si(CH_3)_2$). MS (70 eV): *m*/*z* (%) 515 (8) [M^+], 500 (84) [$M^+ - CH_3$], 485 (22) [$M^+ - 2\ CH_3$], 421 (31) [$M^+ - OTi(CH_3)_2$], 348 (66) [$M^+ - OTi(CH_3)_2 - Si(CH_3)_3$]. Anal. Calcd for $C_{16}H_{48}O_2Si_7Ti$ (517.07): C, 37.16; H, 9.36. Found: C, 36.37; H, 9.34.

$\{SiMe_2[(Me_3Si)_2SiO]_2\}TiBnz_2\cdot THF$ (11). A 1.15 M solution of BnzMgCl (1.7 mL, 1.97 mmol) in THF was added dropwise to a slurry of **7a** (0.5 g, 0.896 mmol) in ether (10 mL) at −78 °C. The heterogeneous mixture was stirred for 15 min and allowed to warm to room temperature within 30 min, after which time the solvent was removed under vacuum. The product was extracted with *n*-pentane and filtered, and the solution was concentrated. Crystallization at −40 °C afforded the title compound **11** as red-orange crystals. Yield: 0.212 g (32%). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.28−6.88 (m, C_6H_5, 10 H), 3.57 (m, THF-OCH_2CH_2, 4 H), 1.41 (m, THF-OCH_2CH_2, 4 H), 2.49 (s, $CH_2C_6H_5$, 4 H), 0.44 (s, $Si(CH_3)_2$, 6 H), 0.28 (s, $Si(CH_3)_3$, 36 H). ^{13}C NMR (C_6D_6, 125.8 MHz): δ 123.5, 128.7, 129.1, 143.9 (C_6H_5), 75.4 (THF-OCH_2CH_2), 67.8 ($CH_2(C_6H_5)$), 25.8 (THF-OCH_2CH_2), −0.1 ($Si(CH_3)_3$), −0.6 ($Si(CH_3)_2$). ^{29}Si NMR INEPT (C_6D_6, 99.4 MHz): δ 15.9 (SiO), −13.0 ($Si(CH_3)_3$), −28.1 ($Si(CH_3)_2$). Anal. Calcd for $C_{32}H_{64}O_3Si_7Ti$ (741.33): C, 51.85; H, 8.70. Found: C, 51.61; H, 8.65.

Reaction of 10 with $B(C_6F_5)_3$ in C_6D_6. A J. Young NMR tube was charged in the glovebox with **10** (30 mg, 0.058 mmol) and $B(C_6F_5)_3$ (30 mg, 0.059 mmol) and dissolved in C_6D_6 (0.5 mL). The progress of the reaction was monitored by ^{1}H NMR spectroscopy, and complete conversion of the starting materials into $SiMe_2[(Me_3Si)_2SiO]_2Ti(C_6F_5)_2$ (**12**) and a mixture of the boranes of formula $MeB(C_6F_5)_2$, $Me_2BC_6F_5$, and BMe_3 (molar ratio 1.0:2.4:1.7) was observed within 5 min, according to the ^{1}H, ^{29}Si, ^{11}B, and ^{19}F NMR spectra. After ca. 6 days, a ratio of approximately 1.0:3.6:0.2 for $MeB(C_6F_5)_2$, $Me_2BC_6F_5$, and BMe_3 was observed. ^{1}H NMR (C_6D_6, 250 MHz): δ 1.35 (m, $BCH_3(C_6F_5)_2$), 0.98 (m, $B(CH_3)_2(C_6F_5)$), 0.74 (s, br, $B(CH_3)_3$), 0.41 (s, $Si(CH_3)_2$, 6 H), 0.21 (s, $Si(CH_3)_3$, 36 H). ^{29}Si (C_6D_6, 59.6 MHz): δ 34.4 (SiO), −11.7 ($Si(CH_3)_3$), −28.5 ($Si(CH_3)_2$). ^{11}B NMR (C_6D_6, 160.5 MHz, external standard $B(OCH_3)_3$): δ 67.8 ($B(CH_3)_3$), 62.2 ($B(CH_3)_2(C_6F_5)$), 52.7 ($BCH_3(C_6F_5)_2$). ^{19}F NMR (C_6D_6, 235.4 MHz): δ −160.9, −149.8, −129.3 ($B(CH_3)_2(C_6F_5)$), −159.8, −145.5, −128.4 ($BCH_3(C_6F_5)_2$), −158.9, −146.9, −116.7 ($Ti(C_6F_5)_2$).

Scheme 1. Synthesis of the Ligand (R = $SiMe_3$)



Reaction of 7a with C_6F_5MgBr. A solution of C_6F_5MgBr in diethyl ether (0.98 M, 0.4 mL, 0.39 mmol) was added to **7a** (0.1 g, 0.18 mmol) dissolved in diethyl ether (3 mL). After the mixture was stirred for 1 day at room temperature, the solvent was removed and the residue extracted twice with *n*-pentane. From this solution, the solvent was removed and the solid raw material analyzed by NMR spectroscopy. The data obtained from this sample are identical with those of **12**.

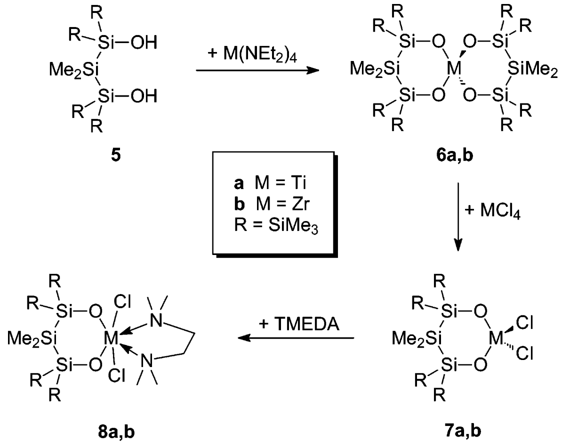
$\{SiMe_2[(Me_3Si)_2SiO]_2(C_6F_5)Ti\}_2O$ (13). A solution of C_6F_5MgBr in diethyl ether (0.98 M, 1.2 mL, 1.18 mmol) was added to **7a** (0.3 g, 0.54 mmol) dissolved in diethyl ether (10 mL). After refluxing of the mixture for 2 days, the solvent was removed, the residue was extracted twice with *n*-pentane, and the combined extracts were concentrated under vacuum. Crystallization from this solution in a freezer afforded the title compound **13** as yellow crystals. Yield: 0.203 g (57%). Mp: 162 °C. ^1H NMR (C_6D_6, 250 MHz): δ 0.46, 0.39 (2s, $Si(CH_3)_2$, 2 × 3 H), 0.27, 0.19 (2s, $Si(CH_3)_3$, 2 × 18 H). ^{13}C NMR (C_6D_6, 75.5 MHz): δ 0.7, −0.4, ($Si(CH_3)_3$), −0.9, −1.1 ($Si(CH_3)_2$). ^{29}Si NMR INEPT (C_6D_6, 59.6 MHz): δ 25.7 (SiO), −12.4 ($Si(CH_3)_3$), −30.5 ($Si(CH_3)_2$). Anal. Calcd for $C_{40}H_{84}F_{10}O_5Si_{14}Ti_2$ (1324.04): C, 36.29; H, 6.39. Found: C, 36.01; H, 6.31.

Results and Discussion

Synthesis of 5 (R = $SiMe_3$). A rather straightforward strategy for the design of the aforementioned 1,3-diolate ligands with an oligosilane backbone involves the use of phenyl-substituted metal silanides in salt metathesis reactions. By treatment with α,ω-dichlorosilanes, a variety of oligosilanes are available, in which the phenyl groups can be converted into hydroxy functionalities using a simple synthetic protocol.

In fact, treatment of Cl_2SiMe_2 with $Ph(Me_3Si)_2SiK$ (**2**), derived from the reaction of Bu^tOK with $Ph(Me_3Si)_3Si$ (**1**),[13a,15] provides easy access to the diphenyloligosilane **3** in high yields.[16] This compound was reacted with 2 equiv of TfOH to yield the ditriflate **4**, which was subsequently hydrolyzed to give almost quantitatively the silanediol **5** as an air-stable, colorless solid that can be synthesized even on a 20-g scale (Scheme 1). The proposed structure of **5** is in full agreement with the NMR, IR, and MS data and the results of an elemental analysis.

Scheme 2. Syntheses of the Complexes **6**−**8**



Synthesis and Reactivity of $\{SiMe_2[(Me_3Si)_2SiO]_2\}MCl_2$ (M = Ti, Zr). A suitable entry into the chemistry of titanium and zirconium silanolate complexes having active sites is the use of highly reactive metal amides. Thus, the reaction of $M(NEt_2)_4$ (M = Ti, Zr) with 2 equiv of **5** leads to the formation of the spirocyclic titanium and zirconium complexes **6a** and **6b**. Without further purification, **6a** and **6b** could be transformed into the corresponding titanium dichloride **7a** and the THF adduct of the zirconium dichloride **7b** in good total yields after treatment with $TiCl_4$ or $ZrCl_4$, respectively (Scheme 2). Both complexes are proven to be Lewis acidic, reacting readily with TMEDA under formation of the hexacoordinated TMEDA adducts **8a** and **8b** almost quantitatively. As expected, the coordinating THF in **7b** is completely replaced by TMEDA according to the NMR spectra.

The proposed structures of the complexes **6a,b**−**8a,b** were confirmed by NMR and MS data and were in full agreement with the results of an elemental analysis. The NMR (^1H, ^{13}C, and ^{19}Si) spectra of all complexes are rather straightforward and show roughly the same features as those observed for the corresponding ligand **5**. Owing to the symmetry in the molecules, the ^1H and ^{13}C NMR spectra exhibit only one signal for the $SiMe_3$ and $SiMe_2$ groups, respectively, and also the ^{29}Si NMR spectra showed only one signal for the $SiMe_3$ silicon atoms.

In addition, the molecular structures of metal dichlorides **7a** and **7b** have been derived from X-ray diffraction data. Suitable single crystals were grown from pentane solutions at room temperature. The results of the X-ray analysis (Figure 1) confirm the expected shielding of the MCl_2 fragments by the trisilane-1,3-diolate ligand and the fact that in **7b** two molecules of THF are coordinated to the Zr atom (Figure 2). Thus, its coordination environment can be regarded as distorted octahedral with the chlorides in axial positions and the two THF molecules in equatorial positions, whereas the geometry of titanium in **7a** is distorted tetrahedral (Figure 1). As expected, the zirconium and titanium are bonded in a chelate fashion [O1−Zr1−O2 96.18(12)° and O1−Ti1−O2 104.25(3)°] to both siloxide groups of the ligand, giving nearly planar six-membered ring systems. The Zr−O [1.924(3) and 1.917(3) Å] and Ti−O [1.7422(6)

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(16) Krempner, C.; Jäger-Fiedler, U.; Mamat, C.; Spannenberg, A.; Weichert, K. *New J. Chem.* **2005**, *29*, 1581.

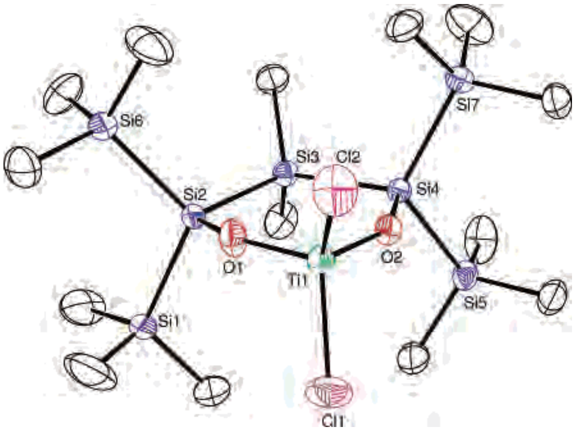


Figure 1. Molecular structure of **7a** in the crystal. The thermal ellipsoids correspond to 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ti1−Cl1 2.2277(3), Ti1−Cl2 2.2376(3), O2−Ti1−O1 104.25(3), O2−Ti1−Cl1 109.65(2), O1−Ti1−Cl1 108.55(3), O2−Ti1−Cl2 110.56(2), O1−Ti1−Cl2 110.05(3), Cl1−Ti1−Cl2 113.364(15).

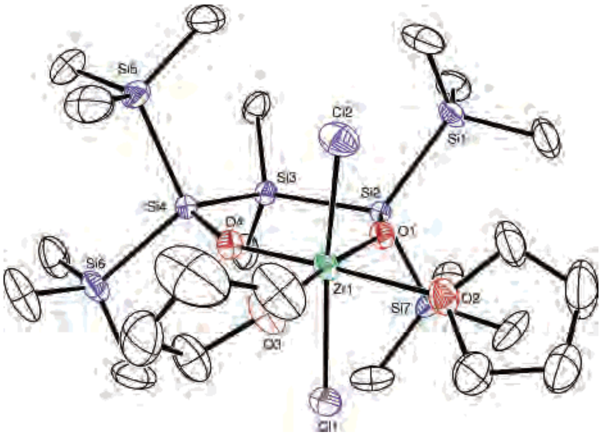
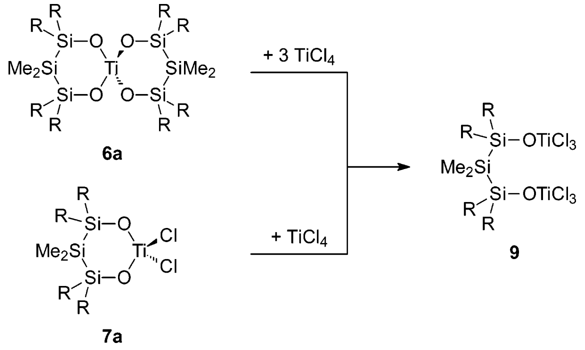


Figure 2. Molecular structure of **7b** in the crystal. The thermal ellipsoids correspond to 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Cl1−Zr1 2.4742(14), Cl5−Zr1 2.4805(13), O1−Si4 1.665(3), O1−Zr1 1.924(3), O2−Si2 1.668(3), O2−Zr1 1.917(3), O3−Zr1 2.315(3), O4−Zr1 2.307(3), Si4−O1−Zr1 147.55(18), Si2−O2−Zr1 148.57(18), O2−Si2−Si3 109.22(11), Si4−Si3−Si2 106.84(6), O1−Si4−Si3 109.35(12), O2−Zr1−O1 96.18(12), O2−Zr1−O4 173.06(13), O1−Zr1−O3 174.38(12), O4−Zr1−O3 83.73(13), Cl1−Zr1−Cl5 162.66(5).

and 1.7451(7) Å] distances within the ring are similar to those found in the closely related dinuclear eight-membered ring complexes $[(OBu^t_2SiO)MCl_2]_2$[17] (M = Ti, Zr), with values being 1.748(2) and 1.746(2) Å for Ti−O as well as 1.930(3) and 1.925(3) Å for the Zr−O bond. Obviously, the ring Zr−O bond lengths are significantly shorter than the Zr−O_{THF} distances [O3−Zr1 2.315(3) Å and O4−Zr1 2.307(3) Å].

Interestingly, when 3 equiv of $TiCl_4$ were reacted with the spirocyclic complex **6a**, a red-orange microcrystalline material, of what was thought to be the dinuclear complex **9**, could be isolated (Scheme 3). The reaction of 1 equiv of $TiCl_4$ with complex **7a** proceeds quite similarly, yielding **9** as the main product. The reactions are quantitative by NMR

Scheme 3. Formation of the Dinuclear Titanium Complex **9**



spectroscopy, and the isolated yields were within 80−85% following crystallization from *n*-pentane. The composition of the thermally stable but moisture-sensitive compound corresponds well to the results of an elemental analysis. However, the mass spectrum shows a highest peak with a molecular weight of 558 being consistent with the formation of **7a**.

Therefore, unambiguous structural characterization was accomplished by single-crystal X-ray crystallography; suitable crystals were grown from *n*-pentane solutions. The results clearly reveal the molecule to be the expected dinuclear complex **9**, which forms a dimeric structure in the solid state (Figure 3). The coordination geometry of the Ti atoms can be described as distorted octahedral. The four titanium trichloride fragments are connected to each other by a sophisticated network of intra- and intermolecular chlorine bridging bonds, with the intramolecular Ti−$Cl_{bridging}$ bonds [Ti1−Cl1 2.5496(4) Å, Ti1−Cl2 2.4051(5) Å, Ti2−Cl1 2.5600(4) Å, and Ti2−Cl2 2.5024(5) Å] being significantly shorter than the intermolecular Ti−$Cl_{bridging}$ bonds Ti2−Cl4a and Ti1−Cl1a with values of 2.7430(4) and 2.7135(4) Å, respectively. The nonbridging Ti−Cl bonds lengths were found to be within the normal range. Similar structural motifs with titanium chlorine bridging bonds in the solid state have been observed previously for [μ-ClTiCl$_2$N(SiMe$_2$Cl)SiMe$_2$NH$_2$] and [μ-ClTiCl$_2$N(SiMe$_3$)SiCl$_2$NH$_2$].[18]

The formation of **9** can be understood as the result of strong interactions of $TiCl_4$ with the oxygen atoms of the

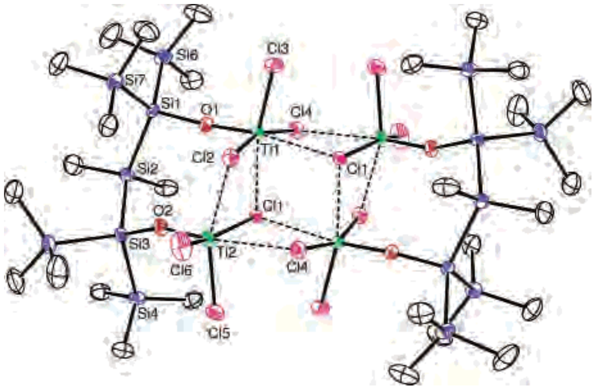


Figure 3. Molecular structure of **9** in the crystal. The thermal ellipsoids correspond to 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ti1−Cl1 2.5496(4), Ti1−Cl1a 2.7135(4), Ti1−Cl2 2.4051(5), Ti1−Cl3 2.2123(5), Ti1−Cl4 2.3273(5), Ti2−Cl1 2.5600(4), Ti2−Cl2 2.5024(5), Ti2−Cl4a 2.7430(4), Ti2−Cl5 2.2263(5), Ti2−Cl6 2.2256(5).

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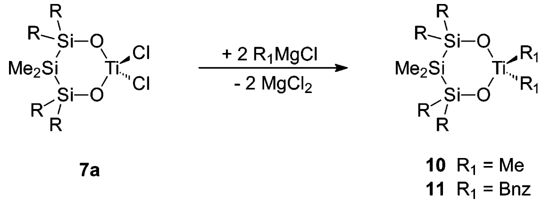
Scheme 4. Syntheses of the Alkyl Complexes **10** and **11**



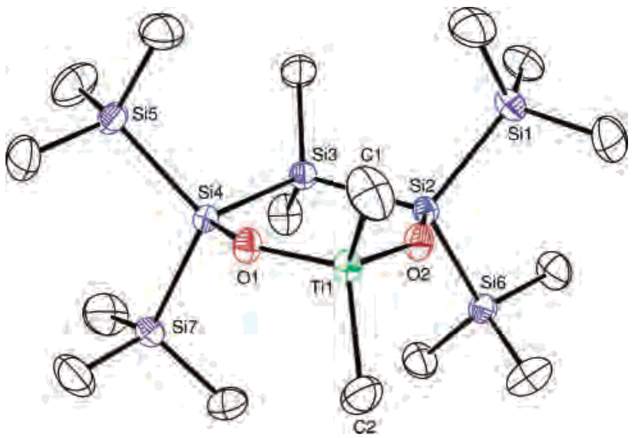


Figure 4. Molecular structure of **10** in the crystal. The thermal ellipsoids correspond to 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ti1−C2 2.0787(18), Ti1−C1 2.0829(19), O2−Ti1−O1 108.19(5), O2−Ti1−C2 107.82(7), O1−Ti1−C2 111.24(7), O2−Ti1−C1 110.62(7), O1−Ti1−C1 109.94(7), C2−Ti1−C1 109.01(9).

strained ring via oxo bridging bonds, which facilitate an insertion of TiCl$_4$ into the Ti−O bond of **7a** in a selective manner. Similar interactions of TiCl$_4$ with spirocyclic **6a** may allow for the formation of unstable di- and trinuclear titanium species, which might be converted rapidly into **6a** and **7a** by ligand distribution reactions and further TiCl$_4$ insertions. The fact that both compounds **6a** and **7a** efficiently undergo ring-opening reaction into derivative **9** even at low temperatures clearly reflects the constraint nature of these six-membered ring complexes relative to larger ring compounds.[19]

Alkylation Reactions of [Me$_2$Si(R$_2$SiO)$_2$]MCl$_2$. The alkyl derivatives of the titanium dichloride **7a** could be synthesized readily via salt metathesis. The complexes **10** and **11** were prepared by treatment with 2 equiv of MeMgBr or BnzMgCl, respectively, in *n*-pentane at −40 °C (Scheme 4). Although NMR spectroscopic investigations of the obtained reaction mixtures indicate the desired complexes to be formed as the main products, the isolated yields after crystallization from concentrated *n*-pentane solutions at −40 °C were low to moderate because of their high solubility in most common organic solvents, including benzene, toluene, diethyl ether, THF, and *n*-pentane. The air- and moisture-sensitive complexes **10** and **11** slowly decompose at room temperature; however, they can be stored without any decomposition for months in a freezer. Attempts to isolate the corresponding zirconium dialkyl derivatives in the pure state failed. In fact, the reaction of the zirconium dichlorides **7b** and **8b** with Grignard reagents at low temperatures led to thermally unstable alkylated species that could not be separated from byproducts arising from M−O bond scissions.

The structures of **10** and **11** were established by means of NMR and MS data and elemental analyses. The TiMe$_2$ group in **10** was identified by a ^{1}H NMR resonance at 0.88 ppm and a ^{13}C NMR signal appearing at 49.2 ppm. The methylene groups of the benzyl ligands in complex **11** exhibit singlets at 2.49 ppm in ^{1}H NMR and at 67.8 ppm in ^{13}C NMR.

The results of an X-ray structure analysis of the titanium dimethyl complex **10** reveal the molecule to be monomeric in the solid state (Figure 4). The coordination geometry of titanium is tetrahedral with an O−Ti−O bite angle of 108.19(5)°. This is remarkable insofar as [Me$_2$Ti(OCBu$^t_3$)(μ-OMe)]$_2$,[20] in which the titanium is protected by the space demand of the tritox ligand, and [Me$_2$Ti(OCHMeCH$_2$Me$_2$CO)]$_2$,[21] a cyclic dialkoxide that has the same ring size as **10**, are dimeric in the solid state. The Ti−C(Me) distances in **10** with 2.0787(18) Å for Ti1−C2 and 2.0829(19) Å for Ti1−C1 were found to be slightly shorter than that of {MeTi[μ-(η^5-C$_5$Me$_4$SiMe$_2$O)]}$_2$(μ-CH$_2$)[22] with 2.121 Å [Ti−C(Me)], which is to our knowledge the only known complex with a Si−O−Ti−Me bond sequence for which X-ray data are available. Furthermore, the Ti−C(Me) bond lengths are only marginally longer than those of the few dimethyltitanium dialkoxides of formula [Me$_2$Ti(OCBu$^t_3$)(μ-OMe)]$_2$[20] with 2.063(10) Å, Me$_2$Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$[23] with 2.069(2) and 2.052(2) Å, and Me$_2$Ti[OC$_6$H$_3$CH$_2$-2-(Bu^t-6-Me-4)]$_2$[24] with 2.031 and 2.090 Å but shorter than those in [Me$_2$Ti(OCHMeCH$_2$Me$_2$CO)]$_2$[21] with 2.110 and 2.183 Å.

Reaction of [Me$_2$Si(R$_2$SiO)$_2$]TiMe$_2$ with B(C$_6$F$_5$)$_3$. With the dimethyltitanium complex **10** in hand, we have investigated its reactivity toward the Lewis acid B(C$_6$F$_5$)$_3$ that is known to abstract alkyl groups from the metal center to form cationic metal species active in olefin polymerization. The reaction was performed at room temperature in a J. Young NMR tube using benzene-*d*$_6$ as the solvent, and the course of the reaction was monitored by ^{1}H NMR spectroscopy. Complex **10** reacted cleanly with B(C$_6$F$_5$)$_3$ (molar ratio 1:1) within minutes, resulting in the quantitative formation of a new complex. However, the reaction did not yield the expected zwitterionic complex [{Me$_2$Si(R$_2$SiO)$_2$}TiMe][MeB(C$_6$F$_5$)$_3$]; rather, the quantitative product of C$_6$F$_5$ group transfer, **12**, was formed together with BMe$_3$, Me$_2$BC$_6$F$_5$, and

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(19) For comparison, hexamethylcyclotrisiloxane (D3), a six-membered ring compound, can readily be polymerized by ring-opening polymerization using anionic or cationic initiators, while octamethylcyclotetrasiloxane (D4), an eight-membered ring, is much less reactive toward ring-opening reactions. See: (a) Terman, L. M.; Klapshina, L. G.; Kurskii, Y. A.; Zislmina, S. S. *Polym. Sci. USSR* **1987**, *29*, 1330. (b) Ziemelis, M. J.; Saam, J. C. *Macromolecules* **1989**, *22*, 2111. (c) Yu, J. M.; Teysslé, D.; Khalifa, R. B.; Boilleau, S. *Polym. Bull.* **1994**, *32*, 35.

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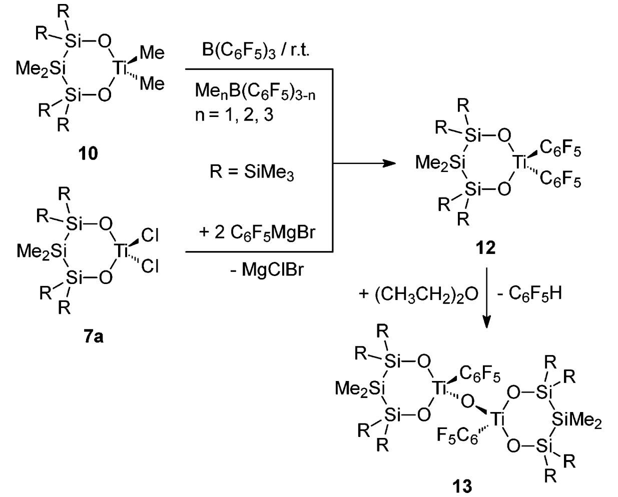
Scheme 5. Formation of **12** and **13**



$MeB(C_6F_5)_2$ in a 1.0:1.7:2.4 ratio, as evidenced by multinuclear NMR spectral data (Scheme 5). Solutions of **12** in C_6D_6 are proven to be fairly stable over a prolonged period of time, and even at higher temperature, no substantial decomposition occurred. Similar C_6F_5 transfer reactions supposed to be responsible for a chemical deactivation of the catalyst precursor in olefin polymerizations have been previously observed.[25] The rapid C_6F_5 transfer observed for complex **10** is in agreement with theoretical calculation indicating lower activation barriers for dialkyl complexes with stronger electron-withdrawing ligands for systems with similar steric properties.[26] The fact that both methyl groups have been replaced smoothly by C_6F_5 groups is somewhat surprising;[27] however, it indicates the high electrophilicity of the titanium center caused by the electron-withdrawing ligand environment.

In addition, the structural interpretation has been confirmed by the independent synthesis of **12** from the titanium dichloride **7a** and 2 equiv of C_6F_5MgBr in diethyl ether at room temperature (Scheme 5). The NMR spectroscopic data of the raw product are identical with those found for **12** derived from the reaction of **10** with $B(C_6F_5)_3$. However, besides **12**, small amounts of a new species could be detected, and with increased reaction time under reflux conditions, the relative concentrations of both compounds continue to change; the new species becomes the major product, whereas the concentration of **12** decreases. The structural characterization of this species was accomplished by single-crystal X-ray crystallography; suitable crystals were obtained from *n*-pentane solutions in a freezer. The analysis of the X-ray data revealed the compound to be the oxo-bridged dinuclear titanium trisilane-1,3-diolate complex **13** in which only one C_6F_5 group is attached to each Ti atom, respectively (Figure 5).

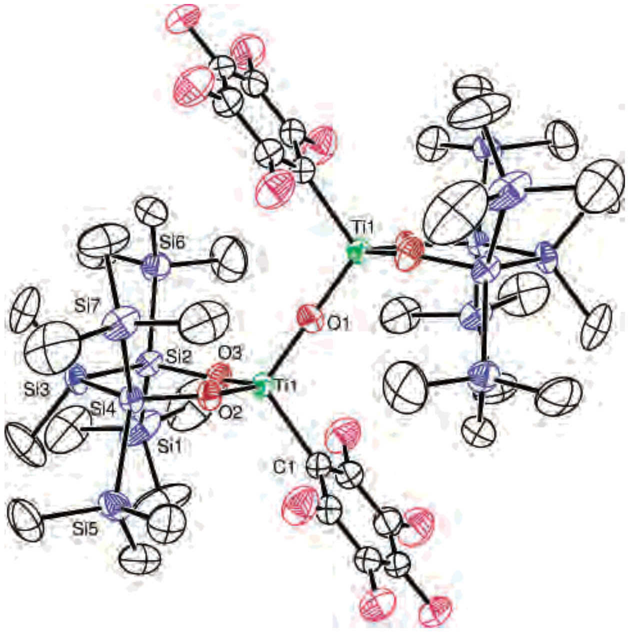


Figure 5. Molecular structure of **13** in the crystal. The thermal ellipsoids correspond to 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ti1−O1 1.8038(3), Ti1−C1 2.1528(16), O2−Ti1−O3 104.99(5), O2−Ti1−O1 112.62(4), O3−Ti1−O1 111.22(4), O2−Ti1−C1 108.40(6), O3−Ti1−C1 109.66(6), O1−Ti1−C1 109.81(4), Ti1#1−O1−Ti1 180.0.

The coordination environment of both Ti atoms is distorted tetrahedral with an O2−Ti1−O3 bite angle of 104.99(5)° and a C1−Ti1−O1 angle of 109.81(4)°. The conformational arrangement of the surrounding atoms along the linear Ti1−O1−Ti1 axis (180°) can be ascribed as anti-periplanar. The Ti1−O1 distance with 1.8038(3) Å was found to be considerably longer than the Ti1−O(ring) distances with values of 1.7577(11) and 1.7601(12) Å, reflecting the steric repulsion of both metal complex fragments to each other. Although the Ti1−C1(C_6F_5) bond length with 2.1528(16) Å is significantly longer than the Ti−C(Me) bond lengths in **10** with 2.0787(18) Å [Ti1−C2] and 2.0829(19) Å [Ti1−C1], it is the shortest Ti−C(C_6F_5) distance observed for C_6F_5-substituted titanium complexes so far [for comparison, see ref 28].

Although the mechanism of formation of the oxo-bridged complex **13** is still unclear, it might be suggested that a titanium-induced ether cleavage has occurred. This probably

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(28) Selected Ti−C(C_6F_5) distances: $[ArN(CH_2)_3NAr]Ti[CH_2B(C_6F_5)_2](C_6F_5)$, 2.191(4) Å;^{24a} $(\eta^5\text{-}C_5H_5)(3,5\text{-}Me_2\text{-}2,6\text{-}Ph_2C_6HO)Ti[CH_2B(C_6F_5)_2](C_6F_5)$, 2.176 Å;^{24b} $[\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(2,6\text{-}Me_2C_6H_3)]\}Ti[CH_2B(C_6F_5)_2](C_6F_5)$, 2.204(5) Å;^{24c} $(\eta^5\text{-}C_5H_5)(Bu^t_2C{=}N)Ti[CH_2B(C_6F_5)_2](C_6F_5)$, 2.263(2) Å;^{24d} $(Bu^t_3P{=}N)_2Ti(C_6F_5)_2$, 2.198(3) and 2.208(3) Å;^{26a} $Cl(C_6F_5)Ti[$*exo,exo*-(η^5-isodiCp)$]_2$, 2.273 Å;^{29} $Cl(C_6F_5)Ti[$*endo,endo*-(η^5-isodiCp)$]_2$, 2.260 Å;^{29} $Cl(C_6F_5)Ti[$*endo,exo*-(η^5-isodiCp)$]_2$, 2.263 Å;^{29} $(NBu_4)_2Ti(C_6F_5)_5$, 2.262(8), 2.257(8), 2.221(7), 2.238(7), and 2.235(6) Å.^{30}

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Table 1. Selected Bond Lengths [Å] and Angles [deg] for the Titanium Complexes **7a**, **9**, **10**, and **13** (L = $[Me_2Si(R_2SiO)_2]$; R = $SiMe_3$)

	$LTiCl_2$ (**7a**)	$LTiMe_2$ (**10**)	$[LTiC_6F_5]_2O$ (**13**)	$L(TiCl_3)_2$ (**9**)
Ti−O	1.7422(6), 1.7451(7)	1.7757(11), 1.7848(11)	1.7577(11), 1.7601(12)	1.7097(10), 1.7262(10)
Si−O	1.7068(7), 1.7114(6)	1.6870(11), 1.6827(11)	1.6962(11), 1.6970(12)	1.7214(10), 1.7205(11)
Si−Si	2.3831(3), 2.3816(3)	2.3825(6), 2.3861(6)	2.3745(6), 2.3808(6)	2.3632(6), 2.3789(6)
O−Ti−O	104.25(3)	108.19(5)	104.99(5)	
Si−O−Ti	145.48(5), 145.97(4)	140.97(6), 144.33(7)	146.17(7), 143.25(7)	167.99(7), 158.27(7)
Si−Si−O	107.75(2), 107.14(2)	107.23(4), 109.22(4)	108.18(4), 107.21(4)	101.98(4), 106.99(4)
Si−Si−Si	107.354(10)	108.10(2)	107.87(2)	113.19(2)

Table 2. Crystal Data Collection and Refinement Details for Crystal Structures[a]

compound	**7a**	**7b**	**9**	**10**	**13**
formula	$C_{14}H_{42}Cl_2O_2Si_7Ti$	$C_{22}H_{58}Cl_2O_4Si_7Zr$	$C_{14}H_{42}Cl_6O_2Si_7Ti_2$	$C_{16}H_{48}O_2Si_7Ti$	$C_{40}H_{84}F_{10}O_5Si_{14}Ti_2$
mol wt	557.91	745.43	747.61	517.07	1324.13
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a, Å	9.3300(2)	10.4226(2)	12.3918(4)	10.0840(3)	12.7493(3)
b, Å	17.7010(4)	22.8237(4)	16.8550(5)	10.1608(3)	12.7949(3)
c, Å	9.9319(2)	17.9217(3)	18.0253(5)	15.8011(5)	12.9031(3)
α, deg	90	90	90	79.403(2)	84.047(1)
β, deg	101.221(1)	105.524(1)	106.144(1)	88.393(2)	76.721(1)
γ, deg	90	90	90	86.560(2)	62.455(1)
V, Å^3	1608.90(6)	4107.72(13)	3616.37(19)	1588.29(8)	1816.34(7)
Z	2	4	4	2	1
ρ, g cm^{-3}	1.152	1.205	1.373	1.081	1.211
cryst size, mm^3	0.55 × 0.40 × 0.25	0.60 × 0.37 × 0.22	0.90 × 0.70 × 0.60	0.80 × 0.43 × 0.33	0.37 × 0.28 × 0.17
2θ limit, deg	80	50	50	50	55
μ, mm^{-1}	0.701	0.625	1.129	0.543	0.509
data, restraints, param	19735, 1, 249	7225, 0, 340	6340, 0, 294	5466, 0, 251	8233, 0, 322
final R1, wR2[b]	0.0271, 0.0697	0.0344, 0.0923	0.0200, 0.0532	0.0242, 0.06688	0.0339, 0.0952

[a] All data sets were collected on a Bruker X8Apex diffractometer system with Mo Kα radiation (λ = 0.710 73 Å, at 173 K). [b] The value of R1 is based on selected data with $F > 4\sigma(F)$; the value of wR2 is based on all data.

may generate oxygen-containing titanium species that rapidly undergo condensation reactions under the formation of Ti−O−Ti bond sequences, finally resulting in the formation of **13**.

Concerning the Electronic Situation in the Ring and the Ligand-to-Metal $\sigma + \pi$ Donation. The fact that M−O distances are shorter for M−O−R groups that have M−O−C angles approaching 180° is generally accepted to be a clue for strong ligand-to-metal π bonding. In the case of silanolate ligands (R = SiR_3), caution must be given because in Si−O−Ti functionalities the silicon is capable of interacting with the oxygen lone pairs in a manner similar to that of titanium. Apart from these interactions, silicon is more electropositive than carbon; thereby, the Si−O−Ti angles are generally expected to be larger than those of C−O−Ti.

As can be seen from Table 1, upon increasing the electronegativity of X in $[Me_2Si(R_2SiO)_2]TiX_2$ in the order $TiMe_2$ (**10**) < $Ti(C_6F_5)O$ (**13**) < $TiCl_2$ (**7a**) < $TiCl_3$ (**9**), the Ti−O distances are shortened, whereas the Si−O bond lengths to some extent are elongated. In contrast, the Si−O−Ti [141−146°], Si−Si−O [107−108°], and Si−Si−Si [107−108°] angles are nearly unaffected by the substitution pattern, owing to the constrained six-membered ring geometry in **7a**, **10**, and **13**. Also the Si−O distances are in a relatively small range with an average value of 1.70 Å, suggesting a weak influence of the group X on the Si−O bond lengths.

In this context, ^{29}Si NMR spectroscopy proved to be a useful tool in studying the electronic situation of the Si−O−TiX_2 bond sequence because the chemical shift of the central silicon is sensitive to the electronegativity of X. In fact, the signals for the central silicon are found to be slightly shifted to lower field upon an increase of the electronegativity of X in the following order $TiMe_2$ < $TiBnz_2$ < $TiOTi(C_6F_5)$ < $Ti(C_6F_5)_2$ ∼ $TiCl_2$ < $TiCl_3$ [14.7 (**10**), 15.9 (**11**), 25.7 (**13**), 34.4 (**12**), 35.7 (**7a**), and 69.1 (**9**) ppm].

Curiously, the Si−O distances are markedly longer and the Ti−O distances are shorter than those of the closely related cyclic complexes $[O(Ph_2SiO)_3]TiClCp^*$,[31] $[O(Ph_2SiO)_3]_2Ti$,[32] $[(OPh_2SiO)_2TiClCp^*]_2$,[33] $[(OBu^t_2SiO)_2TiClCp]_2$,[33] and $[(OBu^t_2SiO)_2TiBr_2]_2$.[17] Similar values have been observed even for the linear complexes $(Ph_3SiO)_4Ti$[34] and $(Ph_3SiO)Ti(Bnz)_2[C_5H_3(SiMe_3)_2]$[35−36] with large Si−O−Ti angles of 170−180°, which are believed to be geometrically optimal for an efficient ligand-to-metal π bonding,

The remarkably longer Si−O distances can mainly be attributed to the specific electronic situation in $[Me_2Si(R_2SiO)_2]TiX_2$ (R = $SiMe_3$), in which the central silicon atoms are surrounded by electropositive silyl groups. These electron-donating groups clearly diminish the capability of the silicon

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to act as a strong π acceptor for oxygen, as was mentioned for the former complexes. The Ti−O distances, which are a function of the electronegativity of X, were found to be fairly short, despite the small Si−O−Ti angles enforced by the constrained ring geometry. From these results, it seems evident that the relatively short Ti−O distances in the new titanium trisilane-1,3-diolates mainly arise from ionic interactions rather than ligand-to-metal π bonding.

Conclusion

The syntheses of the strained six-membered ring complexes $[Me_2Si(R_2SiO)_2]_2M$ (**6a**,**b**), $[Me_2Si(R_2SiO)_2]MCl_2$ (**7a**,**b**), and $[Me_2Si(R_2SiO)_2]MCl_2\cdot TMEDA$ (**8a**,**b**), where R = $SiMe_3$ and M = Ti (**a**), Zr (**b**), derived from the novel bidentate trisilane-1,3-diolate ligand $[Me_2Si(R_2SiO)_2]^{2-}$ (**5**)-H_2, have been reported. In the presence of $TiCl_4$, **6a** and **7a** rapidly undergo a selective ring-opening reaction to $[Me_2Si(R_2SiO)_2][TiCl_3]_2$ (**9**), clearly reflecting the constrained nature of the chelating trisilane-1,3-diolate framework. Especially, complex **7a** has proven to be synthetically useful because it allows for the synthesis of the novel alkyl and aryl complexes $[Me_2Si(R_2SiO)_2]TiR_2$, where R = Me (**10**), Bnz (**11**), and C_6F_5 (**12**). The reaction of complex **10** with $B(C_6F_5)_3$ led to full exchange of both methyl groups by C_6F_5 groups under the quantitative formation of **12**, which can be converted by ether cleavage into **13**.

In addition, the molecular structures of **7a**, **7b**, **9**, **10**, and **13** have been determined by X-ray crystallography. The analysis of the bond parameters within the ring reveals the specific electronic situation of the SiO functionality caused by the surrounding electropositive silyl substituents. A structural comparison of the new titanium trisilane-1,3-diolates with closely related titanium siloxanolates and silanolates suggests the central silicon to be a relatively weak π acceptor for oxygen. Despite the small Si−O−Ti angles due to the constrained ring geometry, the Ti−O distances are fairly short, suggesting ionic Ti−O interactions rather than ligand-to-metal π bonding to be responsible.

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Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre: CCDC 278426 (**7a**), 278427 (**7b**), 278428 (**9**), 278429 (**10**), and 278430 (**13**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033; e-mail deposit@ccdc.cam.ac.uk).

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