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Titanium(IV) alkoxides with Mono- and Bidentate Ligands

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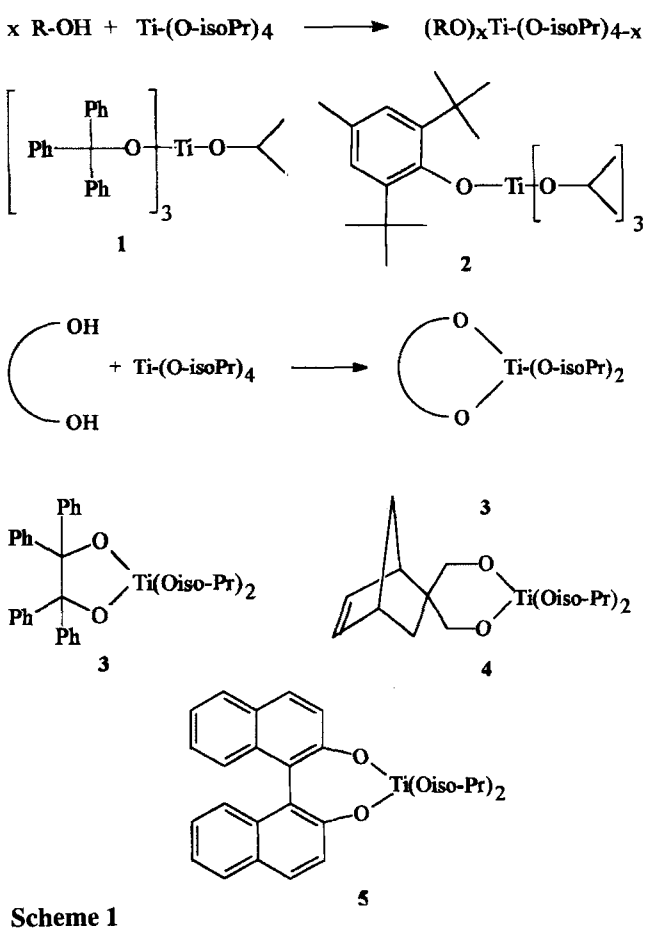
The use of titanium(IV) alkoxides in organic carbanion chemistry is well established [1]. Replacing the counterion, traditionally a main group element, by titanium high stereo- and regioselectivities can be observed [2]. Also in the field of aldol reaction important progress has been made [3]. For our studies in aldol reactions using titanium-ate complexes [4] it was necessary to synthesize several titanium(IV) alkoxides. In order to study the influence of the size of the alkoxy groups on the obtained stereoselectivity of the aldol products, different titanium(IV) alkoxides had to be used. Herein we describe the synthesis and structure of mono-(compounds **1** and **2**, Scheme 1) and bidentate titanium(IV) alkoxides, in the field of bidentate alkoxides especially the synthesis of 5-, 6- and 7-membered titantium(IV) alkoxide rings (compounds **3**, **4** and **5**, Scheme 1).

Results and Discussion

For generating titanium(IV) alkoxides with different substituents several procedures are known [5]. Titanium bound chloride can be substituted by alcohols after deprotonation. Using more acidic alcohols ligand exchange proceeds spontaneously without deprotonation [6]. In some cases formation of titanium alkoxides by substitution of titanium bound halides with the corresponding alcohols is achieved in the presence of molecular sieves [7].

A very efficient method for the preparation of titanium (IV) alkoxides is the „transesterification" of $Ti(OPr)_4$. The reaction is controlled by aceotropic removal of *iso*propanol [8]. Synthesized titanium complexes has been representatively reviewed [5a]. The herein described compounds were synthesized by „transesterification" of titanium(IV) *iso*propoxide with the corresponding alcohols.

The formation of the supposed titanium(IV) alkoxides **1**–**5** (Scheme 1) has been achieved by simply mixing of the corresponding alcohols with titanium(IV) *iso*propoxide in toluene. The formed *iso*-PrOH was removed by azeotropic distillation with toluene. Obviously, the degree of the ligand exchange (formation of $Ti(OPr)_3L$, $Ti(OPr)_2L_2$ or $TiOPrL_3$) depends on steric factors. By reaction of triphenylmethanol with titanium(IV) *iso*propoxide the titanium(IV) *iso*propoxy-tris(triphenylmethoxide) **1** was isolated in good yields. However by treating titanium(IV) *iso*propoxide with 2.6-di-*tert*-butyl-4-methylphenol only the monosubstituted titanium compound **2** was isolated. Even by using an excess of the 2.6-di-*tert*-butyl-4-methylphenol (10 equivalents) in the



Scheme 1

reaction with titanium(IV) *iso*propoxide no titanium(IV) *iso*-propoxy-tris[2.6-di-*tert*-butyl-4-methyl-(phenoxide)] could be observed.

All newly synthesized compounds are stable against air and can be stored under dry conditions at room temperature over a long period of time. The titanates **2–5** melt under decomposition whereas only the titanate **1** shows a sharp melting point. The compounds **1**, **2** and **5** are monomeric in solution, whereas higher aggregation states were observed by NMR experiments for complexes **3** and **4** [9].

The crystal structure analysis of titanium alkoxide **1** revealed the expected geometry of the molecule as shown in Fig. 1.

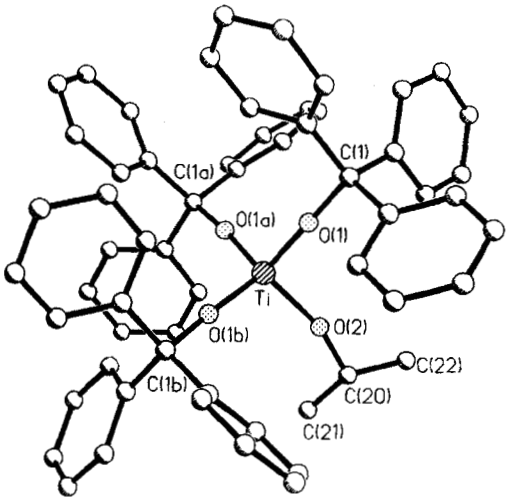


Fig. 1 PLUTON plot of the titanium(IV) alkoxide **1**. All hydrogen atoms have been omited for clarity.

All bond lengths and angles have normal values. The angles at O1 and O2 are 175.1(3)° and 164(2)°, respectively, which deviates significantly from linearity. This deviation coupled with the special position of the molecule in the unit cell (C_3 site symmetry) causes a disordering effect for the *iso*propoxide ligand in the crystal. This partial disorder was analyzed by refinement procedure in SHELXL-93 [10].

The titanium(IV) alkoxide **3** crystallizes in a dimeric form (Fig. 2). The two alkoxide molecules of the unit cell are centrosymmetrical to each other, corresponding to the noncrystallographic inversion centre in (0, 0.4, 0.74). However, the compound crystallizes in the noncentric space group P1 due to the presence of only one molecule toluene per unit cell (Fig. 2).

Titanium(IV) alkoxides with different ligands can be obtained by the described method („transesterification") in crystalline state and good yields. The extend of ligand exchange depends on steric hindrance of the alcohol used.

Experimental

^{1}H and ^{13}C NMR: Bruker WP 200 SY (200 MHz) and Varian Gemini 300 (75 MHz), resp.; chemical shifts are related to tetramethylsilane. — Low-resolution MS (EI) spectra: GC/MS Datensystem HP 5985 B. — Microanalyses: Carlo Erba autoanalyzer 1106.

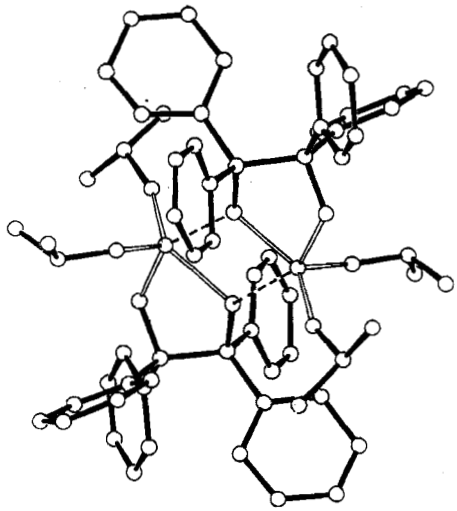


Fig. 2 PLUTON plot of the titanium(IV) alkoxide **3**. All hydrogen atoms have been omited for clarity.

Preparation of the titanates 1–5: General Procedure

25 mmol of the corresponding alcohol or diol were added under inert conditions to 50 ml of anhydrous toluene. 7.5 ml (25 mmol) of Ti(O-*iso*Pr)$_4$ were carefully added at room temperature. The resulting suspension was heated until all solids were dissolved. After 10 h at r. t. the crystals formed were collected by filtration and dried in vacuo.

Isopropoxy tris(triphenylmethoxy)titanium (**1**)

According the general procedure 13.9 g of the titanate **1** were isolated. Yield 62.9%. m.p. 248–251°C.
^{1}H NMR ($CDCl_3$): δ = 1.21(d, J = 6.2 Hz, 6 H, CH_3), 4.63 (sp, J = 6 Hz, 1 H, CH), 7.25–7.60 (45 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 25.78 (CH_3), 79.10 (CH), 94.50 (Ph_3C), 126.65, 127.43, 128.22, 147.83 (aromatic C). – MS (70 eV); *m/z* (%): 807 (8) [M^+ – Ph], 641 (2) [M^+ – Ph_3C], 625 (12) [M^+ – Ph_3CO], 487 (7) [M^+– Ph_3C – 2 × Ph], 366 (4) [M^+ – 2 × Ph_3CO], 243 (100) [Ph_3C^+]. – $C_{60}H_{52}O_4Ti$ (884,9): C 81,45 (calcd. 81,44); H 5,93 (calcd. 5,88).

(2.6-Di-tert-butyl-4-methyl-phenoxy) tris(isopropoxy)titanium (**2**)

According the general procedure 7.1 g of the titanate **2** were isolated. Yield 64.0 %.
^{1}H NMR ($CDCl_3$): δ = 1.48 (d, J = 6.1 Hz, 18 H, CH_3), 1.69 (s, 18 H, CH_3), 2.48 (s, 3H, CH_3), 4.86 (sp, J = 6.1 Hz, 3 H, CH), 7.19 (s, 2H, aromatic H). – ^{13}C NMR ($CDCl_3$): 21.29 (CH_3), 26.34 (CH_3), 30.73 (CH_3), 34.78 (quart. C), 78.13 (CH), 125.24, 127.58, 138.74, 162.26 (aromatic C). – $C_{24}H_{44}O_4Ti$ (444,5): C 64,54 (calcd. 64.86); H 10,03 (calcd. 10,00).

(1.1.2.2-Tetraphenylethan-1.2-diyloxy) bis(isopropoxy)titanium (**3**)

Using the general procedure 8.7 g of the titanate **3** were isolated. Yield 65.7 %.

^{1}H NMR ($CDCl_3$): δ = 1.14 (d, J = 6.1 Hz, 6 H, CH_3), 4.53 (sp, J = 6 Hz, 2 H, CH), 6.8 – 7.7 (m, 20 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 25.29 (CH_3), 79.17 (CH), 80.48 (Ph_2C), 125.28, 125.78, 127.11, 128.21, 128.57, 129.02, 146.09, 147. 41. – MS (70 eV); *m/z* (%): 529 (100) [M^+ – 1], 487(9) [M^+ – C_3H_6], 428 (11) [M^+ – C_3H_7 – OC_3H_7], 167 (100) [Ph_2C^+]. – $C_{32}H_{34}O_4Ti$ (530,5): C 70,08 (calcd. C 72,45); H 5,60 (calcd. 6,46).

(5-Norbornene-2.2-dimethan-diyloxy) bis(isopropoxy) titani- um (**4**)

Using the general procedure 3.4 g of the titanate **4** were isolated. Yield 42.8 %.
^{1}H NMR ($CDCl_3$): δ = 0.75 (br s, 1 H), 1.1 – 1.4 (br s, 3 H), 1.02 (d, J = 6 Hz, 6 H, CH_3), 2.7 (br, 2 H), 4.05 (br, 2H), 4.35 (br, 4 H), 6.05 (br, 2 H). – ^{13}C NMR ($CDCl_3$): δ = 25.93, 26.65 (CH_3), 33.14, 42.71, 45.26, 47.91, 51.12, 77.5 (b), 81.0 (b), 137.01, 137.22. – MS (70 eV); *m/z* (%): 318 (40) [M^+], 303 (100) [M^+–CH_3], 259 (16) [M^+–OC_3H_7], 181 (40) [O=Ti (O_3H_7) (OC_3H_6)]. – $C_{15}H_{26}O_4Ti$ (318,3): C 58,81 (calcd. C 56.60); H 7,77 (calcd. 8,18).

1,1'-Binaphthyl-2.2'-diyloxy) bis(isopropoxy)titanium (**5**)

Using the general procedure 4.5 g of the titanate **5** were isolated. Yield 40 %.
^{1}H NMR ($CDCl_3$): δ = 1.13 (d, J = 6 Hz, 6 H, CH_3), 3.94 (br s, 2 H, CH), 7.1–7.85 (12 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 25.79 (CH_3), 64.58 (CH), 121.12, 123.30, 125.36, 125.60, 126.86, 127.92, 128.81, 130.01, 133.00, 158.85. – MS (70 eV); *m/z* (%): 450 (17) [M^+], 391 (6) [M^+ – OC_3H_7], 349 (22) [M^+ – OC_3H_7 – C_3H_6], 331 (12) [(M^+ – 2 × OC_3H_7) – 1], 269 (100) [M^+ – O=Ti (OC_3H_7) (OC_3H_6)]. – $C_{26}H_{26}O_4Ti$ (450,4): C 68,71 (calcd. 69,34); H 5,17 (calcd. 5,82).

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