

An Internally Coordinated Metalla[14]-crown-5 System with a Pentagonal-dipyramidal Coordination Geometry of the Central Titanium Atom

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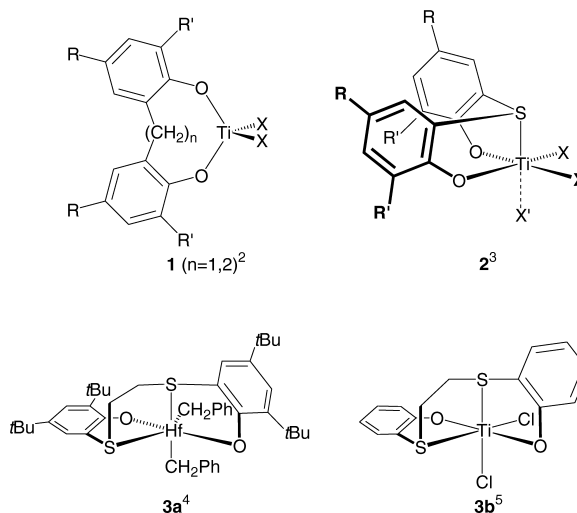
Treatment of the dilithiated dibenzotetraethyleneglycol reagent $[(o\text{-C}_6\text{H}_4\text{OLi})\text{-(OCH}_2\text{CH}_2)_2\text{O-(}o\text{-C}_6\text{H}_4\text{OLi)}]$ (**5**) with $\text{TiCl}_4 \cdot 2 \text{ THF}$ gave the corresponding metal complex $[\{(o\text{-C}_6\text{H}_4\text{O})\text{-(OCH}_2\text{CH}_2)_2\text{O-(}o\text{-C}_6\text{H}_4\text{O)}\}\text{TiCl}_2]$ (**6**). The X-ray crystal structure analysis of **6** revealed that all five oxygen atoms are located in one plane and bonded to titanium in a pentagonal-dipyramidal geometry with the two chloride ligands being oriented trans to each other in the apical positions.

Key words: Titanium Complex, Chelate Ligand, Metalla-Crown Ether, Aryloxy-Ligand

Introduction

Bis(aryloxy) MX_2 complexes of the Group 4 metals are interesting substrates for generating active catalysts for olefin polymerization. They often show a high tendency for oxygen-metal backbonding which leads to the observation of large carbon-oxygen-metal angles and short oxygen-metal bonds. In some of their properties the $(\text{ArO})_2\text{MX}_2$ systems show a remote resemblance with the bent metallocene complexes of the Group 4 elements [1].

Complexes of bridged bis(aryloxy) ligands have been of particular interest, since some such systems provide the basis of very active catalysts. They exhibit quite special structural features. The unfunctionalized $(\text{-CH}_2\text{-})_n$ -bridged systems (**1**, see Scheme 1) show distorted tetrahedral coordination geometries at the metal center, sometimes further distorted by additional donor ligands [2]. The structure of the sulfide-bridged systems **2** in contrast is dominated by a pronounced intramolecular chalcogen-metal interaction that usually leads to pseudooctahedral metal environments, where the sixth ligand originates from dimer formation or the addition of an external donor ligand [3]. Mononuclear pseudooctahedral coordination is exhibited by the $\text{-S-CH}_2\text{-CH}_2\text{-S-}$ -linked systems **3** (and probably also by their oxygen analogues). In the systems **3** the phenolic oxygen atoms are trans-positioned at the metal cen-



Scheme 1.

ter, whereas the sulfur donors are in *cis*-positions [4, 5]. The systems **1** to **3** all have in common that their specific coordination geometries have resulted in the presence of the two X-ligands in *cis*-positions to each other (see Scheme 1).

This posed the question of what would happen if a third sulfur or oxygen donor be placed inside the bridge. Would one donor atom of *e.g.* the $\text{-OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O-}$ linker just not be involved in the coordination to the metal [to preserve the favourable octahedral coordination geometry with a *cis*

* X-ray crystal structure analysis.

(X[−])₂ ligand orientation] or would a completely different coordination scheme be enforced? We have prepared such an example and structurally characterized it. Its X-ray crystal structure analysis has revealed a novel type of coordination for such a (L_n)TiCl₂ complex.

Results and Discussion

The -OCH₂CH₂OCH₂CH₂O- bridged bis(phenol) **4** was prepared according to a literature procedure [6]. In principle its subsequent reaction with TiCl₄ might have been attempted by direct treatment of the Group 4 metal halide with the rather acidic phenolic reagent, similarly as we had done it in the case of the synthesis of complex **3b** (see Scheme 1) [5]. In this case, we have, however, decided to follow the alternative two-step procedure. Treatment of **4** with *n*-butyl lithium in hexane gave **5**. Its subsequent reaction with TiCl₄ in THF, followed by extraction with dichloromethane and crystallization at low temperature gave complex **6** as a dark red crystalline material (*ca.* 60% isolated, see Scheme 2). Complex **6** shows the NMR features of two symmetry equivalent phenylene groups [¹³C: δ 156.4 (C1), 150.7 (C6), 124.1, 124.2, 110.8, 113.0, (C2–C5)] and the typical resonances of the bridging -OCH₂CH₂OCH₂CH₂O- moiety [¹H: δ 4.70, 4.40 (m, each 4H); ¹³C: δ 71.7, 66.9 (C8, C7)].

Single crystals of complex **6** were obtained from dichloromethane, and also from the neutral starting material that was obtained as a mono-hydrate (**4**·H₂O) from toluene. A view of the molecular geometry of (**4**·H₂O) is depicted in Fig. 1. Unfortunately, the core of the molecule shows a 1:1 positional disorder. It is, however, evident that the framework is held together in a shallow bowl shaped arrangement by hy-

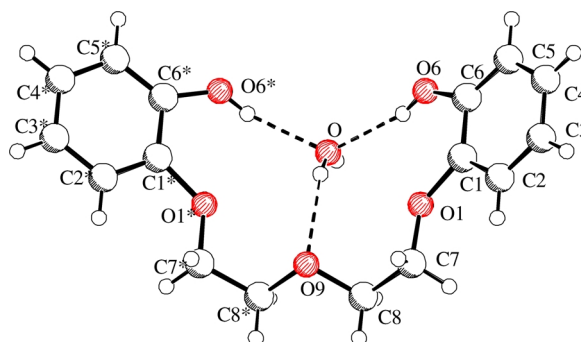
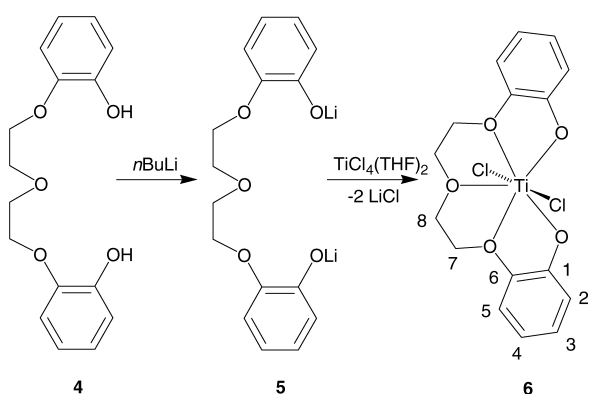


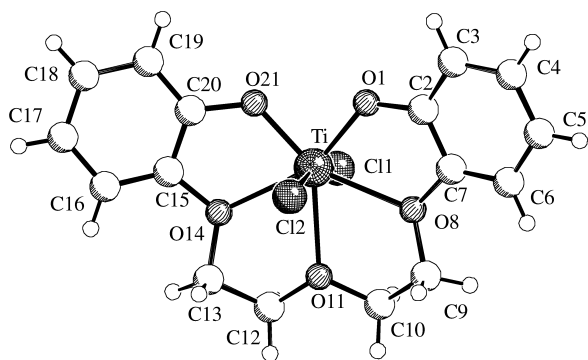
Fig. 1. A view of the molecular structure of (**4**·H₂O) featuring three hydrogen bonds to the centrally located water molecule. Selected bond lengths (Å) and angles (°): C6–O6 1.307(12), C6–C1 1.408(5), C1–O1 1.469(9), O1–C7 1.440(8), C7–C8 1.520(10), C8–O9 1.451(9), O[⋯]O6 2.756(11), O[⋯]O1 3.070(8), O[⋯]O9 3.169(7); O6–C6–C1 106.8(4), C6–C1–O1 127.4(4), C1–O1–C7 126.5(6), O1–C7–C8 108.3(6), C7–C8–O9 108.7(5), C8–O9–C8* 109.6(7).

drogen bridges between the phenolic HO(6)/HO(6*)[−] hydroxyl group and a centrally located H₂O molecule plus an additional hydrogen bond between H₂O and the central ether oxygen (O9) of the bridge.

The titanium complex **6** attains a related structure in the crystal (see Fig. 2). The structural framework of complex **6** can be described as distorted pentagonal-dipyramidal. The five ligand oxygen atoms are arranged close to coplanar in the central plane while the two chloride ligands occupy the remaining apical positions. The positions of the oxygen atoms in the meridial plane differ not much from regular pentagonal. Actually, the O21–Ti–O14 (72.84(9)°) and O1–Ti–O8 (71.63(9)°) angle are only marginally different from the ideal angle of 72°, whereas the adjacent O14–Ti–O11 (66.93(8)°) and O8–Ti–O11 (65.71(8)°) angles are slightly smaller. Consequently, the O21–Ti–O1 angle (82.81(10)°) is larger. The Ti–O21 (1.855(3) Å) and Ti–O1 (1.865(2) Å) bonds are short, as expected. The remaining Ti–O8 (2.315(2) Å), Ti–O14 (2.272(2) Å) and Ti–O11 (2.317(2) Å) linkages are all longer, but among themselves within a very close range. The C10–O11–C12 angle is in the expected range at 110.9(3)°. The C7–O8–C9 (118.5(3)°) and C13–O14–C15 (119.4(3)°) angles are markedly larger, as are the C2–O1–Ti (126.5(2)°) and C20–O21–Ti (125.9(2)°) angles. The chloride ligands are arranged trans to each other and thus positioned above and below the central O₅Ti plane. The Ti–Cl vectors (at 2.332(1) Å and 2.333(1) Å) are bent slightly toward the closed section of the ligand framework (Cl1–Ti–Cl2 164.44(4)°).



Scheme 2.



Complex **6** favours a structure that is characterized by a substantial bonding contribution of all five oxygen atoms to the titanium atom. Apparently, alternatives with a lower coordination number are disfavoured. Utilization of strong oxygen to metal backbonding (as it was observed in related metallocene examples [7]) does apparently not provide a sufficient energetic compensation in this overall situation. A similar tendency to form complex geometries with increased coordination number was previously observed *e.g.* in some zirconium halide complexes [8] and in a ring-opening product of a crown ether with ZrCl_4 [9]. We are curious to see whether the characteristic pentagonal-dipyramidal structure of complex **6** will be retained in the formation of organometallic derivatives or if other structural types will emerge from these systems.

All reactions and handling of the metal complexes were carried out under argon in Schlenk-type glassware or in a glovebox. Solvents were dried and distilled prior to use. The ligand system (**4**) [6] and the $\text{TiCl}_4(\text{THF})_2$ reagent [10] were prepared as described in the literature. NMR spectra were recorded on a Bruker AMX 400 (^1H : 400 MHz; ^{13}C : 100 MHz) spectrometer. Most assignments were confirmed by 2D NMR spectra. The following instruments were used for additional physical characterization: melting points: DSC 2010 (TA instruments); elemental analysis: Foss

Preparation of 5: A sample of **4** (0.55 g, 1.9 mmol) was dissolved in dry tetrahydrofuran and cooled to -78°C . *n*-Butyllithium (2.4 ml of a 1.6 M solution in hexane) was added dropwise to the stirred solution. The reaction mixture was allowed to warm to room temperature and the solvent was then removed in vacuo. The product was obtained as a white powder (0.56 g, 98% yield).

M.p. 216 °C. – ¹H NMR (400 MHz, C₆D₆/C₄D₈O, 5/1): δ = 3.09 (m, 4 H, 8-H), 3.64 (m, 4 H, 7-H), 6.59 (td, *J* = 7.5 Hz, 1.4 Hz, 2 H, 4-H), 6.70 (dd, *J* = 7.5 Hz, 1.4 Hz, 2 H, 5-H), 6.86 (dd, *J* = 7.5 Hz, 1.4 Hz, 2 H, 2-H), 6.97 (td, *J* = 7.5 Hz, 1.4 Hz, 2 H, 3-H). – ¹³C NMR (100 MHz, C₆D₆/C₄D₈O, 5/1): δ = 65.1 (C-7), 66.5 (C-8), 111.2 (C-4), 111.5 (C-5), 118.1 (C-2), 121.5 (C-3), 149.5 (C-6), 157.4 (C-1). – ¹H/¹H GCOSY (400 MHz/400 MHz, C₆D₆/C₄D₈O, 5/1): δ = 3.09/3.64 (8-H/7-H), 3.64/3.09 (7-H/8-H), 6.59/6.70, 6.97 (4-H/5-H, 3-H), 6.70/6.59 (5-H/4-

H), 6.86/6.97 (2-H/3-H), 6.97/6.59, 6.86 (3-H/4-H, 2-H). – $^1\text{H}/^{13}\text{C}$ GHSQC (400 MHz/100 MHz, $\text{C}_6\text{D}_6/\text{C}_4\text{D}_8\text{O}$, 5/1): $\delta = 3.09/66.5$ (8-H/C-8), 3.64/65.1 (7-H/C-7), 6.59/111.2 (4-H/C-4), 6.70/111.5 (5-H/C-5), 6.86/118.1 (2-H/C-2), 6.97/121.5 (3-H/C-3). – $\text{C}_{16}\text{H}_{16}\text{Li}_2\text{O}_5$ (302.18): calcd. C 63.60, H 5.34; found C 63.83, H 5.77.

Synthesis of complex 6: A mixture of 0.50 g (1.7 mmol) of the dilithium salt **5** and 0.55 g (1.7 mmol) of the titantium tetrachloride / tetrahydrofuran adduct was cooled to -78°C and then dissolved in 40 ml of dry THF. The dark red reaction mixture was allowed to warm to room temperature and the solvent was removed in vacuo. Treatment of the residue with 40 ml of dichloromethane gave a red suspension, the precipitate was removed by filtration. The clear filtrate was concentrated in vacuo to one tenth of its original volume and the product precipitated at -25°C as dark red crystals (0.41 g, 59 % yield).

M.p. 253°C . – ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 4.40$ (m, 4 H, 8-H), 4.70 (m, 4 H, 7-H), 6.70 (m, 2 H, 5-H), 7.02–7.10 (m, 6 H, 2,3,4-H). – ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 66.9$ (C-7), 71.7 (C-8), 110.8 (C-4), 113.0 (C-5), 124.1 (C-2), 124.2 (C-3), 150.7 (C-6), 156.4 (C-1). – $^1\text{H}/^1\text{H}$ GCOSY (400 MHz/400 MHz, CD_2Cl_2): $\delta = 4.40/4.70$ (8-H/7-H), 4.70/4.40 (7-H/8-H),

6.70/7.02–7.10 (5-H/2,3,4-H), 7.02–7.10/6.70 (2,3,4-H/5-H). – $^1\text{H}/^{13}\text{C}$ GHSQC (400 MHz/100 MHz, CD_2Cl_2): $\delta = 4.40/71.7$ (8-H/C-8), 4.70/66.9 (7-H/C-7), 6.70/113.0 (5-H/C-5), 7.10–7.02/124.2, 124.1, 110.8 (2,3,4-H/C-3, C-2, C-4). – $\text{C}_{16}\text{H}_{16}\text{Cl}_2\text{O}_5\text{Ti}$ (407.07): calcd. C 47.21, H 3.96; found C 46.82, H 3.86.

X-ray crystal structure analysis of 6: formula $\text{C}_{16}\text{H}_{16}\text{Cl}_2\text{O}_5\text{Ti}\cdot\text{CH}_2\text{Cl}_2$, $M = 492.01$, red crystal $0.20 \times 0.10 \times 0.03$ mm, $a = 7.270(1)$, $b = 8.725(1)$, $c = 32.593(1)$ Å, $\beta = 94.05(1)^\circ$, $V = 2062.2(4)$ Å³, $\rho_{\text{calcd.}} = 1.585$ g cm⁻³, $\mu = 9.58$ cm⁻¹, empirical absorption correction ($0.831 \leq T \leq 0.972$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and ϕ scans, 8291 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin \theta)/\lambda] = 0.66$ Å⁻¹, 4876 independent ($R_{\text{int}} = 0.061$) and 3012 observed reflections [$I \geq 2\sigma(I)$], 244 refined parameters, $R = 0.057$, $wR^2 = 0.104$, max. residual electron density 0.37 (–0.55) e Å⁻³, hydrogens calculated and refined as riding atoms.

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