Structural Features of a Sulfur-Containing Group 4 Metalla[11]-crown-4 Derivative

Alexander Snell[§], Gerald Kehr, Birgit Wibbeling, Roland Fröhlich[#], and Gerhard Erker

Organisch-Chemisches Institut der Universität Münster,
Corrensstraße 40, D-48149 Münster, Germany

Reprint requests to Prof. Dr. G. Erker. E-mail: erker@uni-muenster.de

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Treatment of the ligand system (o-C_6H_4OH)–S–CH_2–CH_2–S–(o-C_6H_4–OH) (**2a**) with $TiCl_4$ gave the metalla-crown ether derivative [(–S–CH_2–CH_2–S–)(o-$C_6H_4O)_2$]$TiCl_2$ (**5a**). Complex **5a** was characterized by an X-ray crystal structure analysis. It showed a pseudo-octahedral structure with both sulfur atoms being *cis*-coordinated to the metal center. The chloride ligands are also *cis*-positioned, whereas the remaining two Ti−oxygen bonds are *trans* to each other to complete the distorted octahedral coordination geometry. The reaction of **2a** with $ZrCl_4$ gave the analogous complex **5c**. The related ligand system (o-C_6H_4OH)–O–CH_2–CH_2–O–(o-C_6H_4OH) (**2b**) was doubly deprotonated by treatment with butyl lithium and then reacted with $TiCl_4$ to yield the complex [(–O–CH_2–CH_2–O–)(o-$C_6H_4O)_2$]$TiCl_2$ (**5b**).

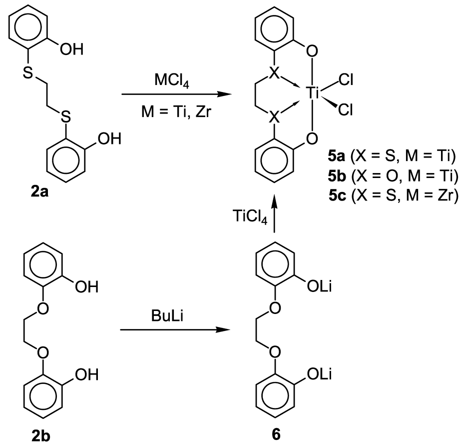
Key words: Titanium Phenoxide Complexes, Internal Coordination, Thioether Chelate Ligands

Introduction

Crown ethers have a wide spread use in chemistry due to their pronounced ability for selective metal cation complexation [1]. If one of the hydrocarbyl moieties is exchanged by an electrophilic metal center then the interesting possibility arises that an internal coordination to the metal center may occur. In the case of incorporation of *e. g.* a [Ti]Cl_2 or [Zr]Cl_2 unit into the crown ether framework this could lead to coordination geometries at the group 4 metal that might be favorable for catalytic purposes. Such systems could provide new members in a series of donor-stabilized phenoxide group 4 derived olefin polymerization catalysts [2], similar to the systems described by *e.g.* Kakugo [3], Okuda [4], and others [5]. We have prepared a small series of such oxygen and sulfur-containing systems and characterized one example by X-ray diffraction.

Results and Discussion

The synthesis of the ligand system **2a** was carried out in analogy to a literature procedure [6] by treatment of o-mercaptophenol with 1,2-dibromoethane in refluxing ethanol under basic conditions. The product (**2a**) was isolated in *ca.* 40% yield. The corresponding oxygen-containing ligand **2b** was prepared selectively in a slightly more complicated way following a procedure published by Vögtle *et al.* [7]. One hydroxy group of catechol was selectively protected by benzylation. The reagent 2-(benzyloxy)phenol (**3**) was then treated with 1,2-dibromoethane in EtOH/KOH followed by hydrogenolytic removal of the benzyl protecting group to give **2b** in a combined yield of *ca.* 50%.



Scheme 1.

Both the neutral ligand systems **2a** (X = S) and **2b** (X = O) were characterized by X-ray diffrac-

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[#] X-ray crystal structure analyses;
[§] this work is part of Alexander Snell's doctoral thesis.

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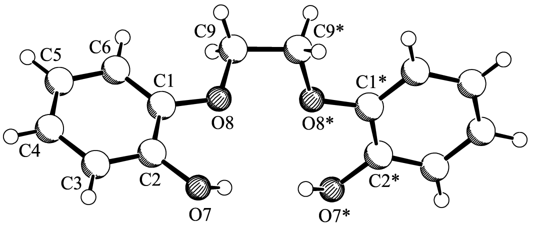

Fig. 1. A projection of the molecular structure of **2b** in the crystal. Selected bond lengths (Å) and angles (°): C1-O8 1.368(3), C1-C2 1.393(4), C2-O7 1.372(3), O8-C9 1.416(3), C9-C9* 1.497(5), H7$\cdots$O8 2.21, H7$\cdots$O7* 2.27; O7-C2-C1 119.8(3), C2-C1-O8 114.2(3), C1-O8-C9 117.8(2), O8-C9-C9* 108.0(2), O7-H7$\cdots$O8 111.8, O7-H7$\cdots$O7* 149.2.

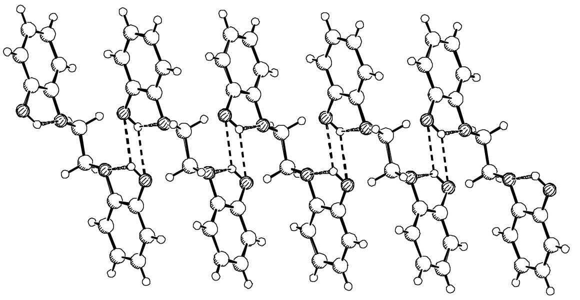

Fig. 2. A view of the layered superstructure made by connecting the molecules of **2b** in the solid state by hydrogen bridges.

tion. Single crystals of **2b** were obtained from chloroform/petrolether. Molecules of **2b** adopt a C_2-symmetric conformation in the crystal, that is characterized by a dihedral angle θ (O8–C9–C9*–O8*) of 66.9(4)°. The almost ideal gauche arrangement of the two catecholate subunits at the bridging $-CH_2-CH_2-$ moiety brings all four oxygen atoms relatively close together (see Fig. 1). The C1–O8–C9 angle amounts to 117.8(2)°. The oxygen atoms O7 und O7* both have hydrogens bonded, that are used to connect the single molecules of **2b** by hydrogen bridges with their neighboring **2b** units to form a layered superstructure (see Fig. 2) [8].

Single crystals of the sulfur compound **2a** were obtained from a 1:3 petrolether/chloroform mixture. The molecular structure of **2a** is characteristically different from the oxygen analogue. The compound attains a conformation in the solid state that shows an antiperiplanar arrangement of the two sulfur substituents at the bridging ethylene unit (dihedral angle θ (S2–C1–C1*–S2*) = 180.0°). The angle at the sulfur atoms is 100.7(1)°, which is in the expected range [9]. The terminal arene substituents are markedly rotated from the central S_2C_2 plane (dihedral angle C1*–C1–S2–C3: 64.8(3)°). A view of the molecular structure of compound **2a** is given in Fig. 3.

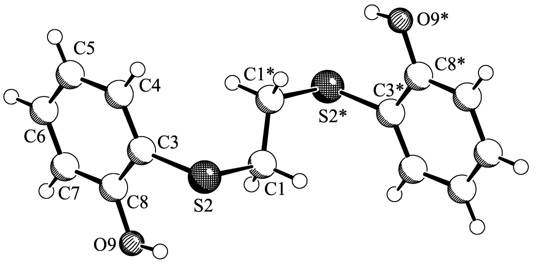

Fig. 3. Molecular structure of **2a**. Selected bond lengths (Å) and angles (°): C3-S2 1.774(2), C3-C8 1.397(3), C8-O9 1.353(2), S2-C1 1.840(3), C1-C1* 1.504(5); O9-C8-C3 123.0(2), C8-C3-S2 119.0(2), C3-S2-C1 100.7(1), S2-C1-C1* 110.9(3).

A solution of **2a** (X = S) in dichloromethane was reacted with titanium tetrachloride at room temperature. The mixture turned orange within a few minutes and an orange precipitate of complex **5a** was formed. Complex **5a** was isolated in $>85\%$ yield from the reaction mixture. In THF-d_8 solution the product exhibits an ^{1}H NMR singlet at $\delta = 3.12$ (s, 4H) [corresponding ^{13}C NMR signal at $\delta = 41.1$] of the $-S-CH_2-CH_2-S-$ bridge aside from an ^{1}H NMR ABCD pattern of signals ($\delta = 7.49$, 7.39, 7.01, 6.93) of the pair of unsymmetrically substituted phenylene units [corresponding ^{13}C NMR features at $\delta = 134.0$, 133.1, 125.0, 123.7, ipso-carbon signals at $\delta = 158.5$(C1) and 116.5(C2)].

Single crystals of complex **5a** (X = S) were obtained from a dichloromethane solution at −30 °C. Complex **5a** shows a distorted octahedral coordination geometry around the central titanium atoms, featuring bonds to both oxygen *and* both sulfur atoms (similarly as described by Okuda *et al.* in related complexes [10]) in addition to a pair of remaining chlorides. The two chloride ligands and the sulfur atoms are oriented in one plane. Both oxygen atoms are coordinated *cis* to these, *i.e.* they are occupying the pseudo-apical positions in this arrangement. The O11–Ti–O28 angle consequently is very large at 158.07(8)°, being ca. 22° away from the ideal value of 180°. This deviation is even smaller for the other two *trans*-orientations: Cl2–Ti–S18 164.88(3)° and Cl1–Ti–S21 164.49(3)°. The overall geometry of **5a** is chiral and close to C_2-symmetric (but not crystallographically) with a gauche-like conformation of the S21–C20–C19–S18 bridge (dihedral angle −57.1(2)°). Eleven out of the twelve *cis*-angles

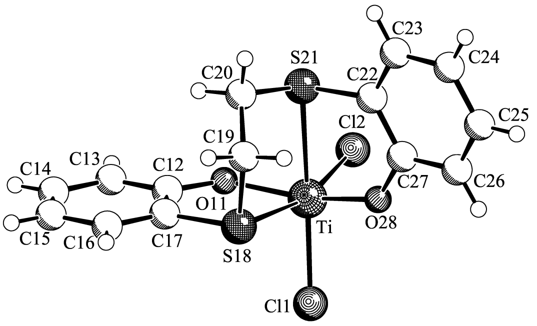

Fig. 4. Molecular structure of the titanium complex **5a**. Selected bond lengths (Å) and angles (°): Ti-Cl1 2.251(1), Ti-Cl2 2.257(1), Ti-O11 1.882(2), Ti-O28 1.861(2), Ti-S18 2.651(1), Ti-S21 2.643(1), O11-C12 1.352(3), C17-S18 1.778(2), S18-C19 1.823(3), C19-C20 1.510(4), C20-S21 1.817(3), S21-C22 1.776(3), C27-O28 1.349(3); Cl1-Ti-Cl2 106.10(3), Cl1-Ti-O11 99.26(6), Cl1-Ti-O28 94.97(6), Cl1-Ti-S18 87.57(3), Cl1-Ti-S21 164.49(3), Cl2-Ti-O11 93.96(6), Cl2-Ti-O28 98.04(6), Cl2-Ti-S18 164.88(3), Cl2-Ti-S21 88.24(3), O11-Ti-O28 158.07(8), O11-Ti-S18 77.14(5), O11-Ti-S21 85.32(6), O28-Ti-S18 86.94(6), O28-Ti-S21 76.81(5), S18-Ti-S21 78.96(2), Ti-O11-C12 131.6(2), Ti-O28-C27 133.1(2), Ti-S18-C17 94.65(8), Ti-S18-C19 105.58(9), Ti-S21-C22 94.97(9), Ti-S21-C20 105.22(8), C17-S18-C19 101.4(1), C22-S21-C20 101.4(1), S18-C19-C20 113.4(2), S21-C20-C19 113.7(2).

at the pseudo-octahedral titanium center vary between 76.81(5)° (O28–Ti–S21) and 99.26(6)° (O11–Ti–Cl1). The Cl1–Ti–Cl2 angle is larger (106.10(3)°), being in the typical range of Cl–M–Cl angles at the group 4 bent metallocene dichlorides [11]. The S21–Ti–S18 angle is much smaller (78.96(2)°).

In **5a** the titanium-oxygen bond lengths are rather short (Ti–O11 1.882(2) Å, Ti–O28 1.861(2) Å) and the bond angles at oxygen are markedly enlarged (C12–O11–Ti 131.6(2)°, C27–O28–Ti 133.1(2)°), which may indicate some residual oxygen–Ti π-interaction [12]. The Ti–S21 and Ti–S18 bond lengths are found at 2.643(1)Å and 2.651(1)Å, respectively, which is in the expected range of a titanium-SR_2 coordination [13]. The sulfur atom coordination is pyramidal. Typical bond angles at S21 are: 94.97(9)° (C22–S21–Ti), 105.22(8)° (C20–S21–Ti) and 101.4(1)° (C22–S21–C20; sum of the bonding angles at S21: 301.6°, the bonding features at S18 are analogous).

The all-oxygen analogue **5b** (X = O) was prepared in a slightly different way. First, the neutral ligand system (**2b**) was doubly deprotonated at the phenolic OH groups by treatment with butyl lithium. The dilithio compound (**6**) was isolated as a solid, which was then subsequently treated with 0.5 molar equivalents of $TiCl_4$ in diethyl ether to yield **5b** ($>$ 90% isolated). Complex **5b** shows similar spectroscopic features as **5a** (**5b**: ^{1}H NMR: $\delta = 4.39$ (s, 4H, –OCH_2–CH_2O–). The complex **5b** shows ^{13}C NMR features of the pair of *o*-phenylene moieties at $\delta = 161.0$ (C1), 143.3 (C2), 121.8, 119.3, 114.4, 112.1 (C3–C6) and 67.2 (OCH_2CH_2O). We assume a similar structure as found for **5a**, although this must remain to be proven by an X-ray crystal structure analysis. Treatment of **2a** with a suspension of $ZrCl_4$ in dichloromethane gave the corresponding complex **5c** (85% isolated, for details see the Experimental Section).

Our study has shown that metalla-crown ether and -thioether derivatives, such as the complexes **5**, are readily available. It would be interesting to learn if some specific organometallic chemistry can be developed based on such systems, *e.g.* by substituting the pair of chloride ligands by suitable hydrocarbyl or conjugated diene ligands. Such studies are currently being carried out in our laboratory.

Experimental Section

Reactions involving metal-containing compounds were carried out under argon using Schlenk-type glassware or in a glove box. Solvents, including deuterated solvents used for NMR spectroscopy, were dried and distilled under argon prior to use. The known compounds **2a** and **2b** were prepared analogously as described in the literature [6, 7]. X-ray crystal structure analyses: Data sets were collected with Enraf Nonius CAD4 or Nonius Kappa CCD diffractometers, the latter one equipped with a rotating anode generator Nonius FR591. The following programs were used: Data collection EXPRESS (Nonius B.V., 1994) and COLLECT (Nonius B.V., 1998), data reduction MolEN (K. Fair, Enraf-Nonius B.V., 1990) and Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, **1997**, *276*, 307 – 326), absorption correction for CCD data SORTAV (R.H. Blessing, *Acta Cryst.* **1995**, *A51*, 33 – 37; R. H. Blessing, *J. Appl. Cryst.* **1997**, *30*, 421 – 426), structure solution SHELXS-97 (G. M. Sheldrick, *Acta Cryst.* **1990**, *A46*, 467 – 473), structure refinement SHELXL-97 (G. M. Sheldrick, Universität Göttingen, 1997), graphics SCHAKAL (E. Keller, Universität Freiburg, 1997).

*X-ray crystal structure analysis of **2a***

Formula $C_{14}H_{14}O_2S_2$, $M = 278.4$, colourless crystal $0.45 \times 0.15 \times 0.15$ mm, $a = 5.267(1)$, $b = 9.625(1)$, $c = 13.133(1)$ Å, $\beta = 100.79(1)$, $V = 654.0(2)$ Å^3, $\rho_{\text{calc}} = 1.414$ g cm^{-3}, $\mu = 36.13$ cm^{-1}, empirical absorption correction *via* ψ scan data ($0.293 \leq T \leq 0.613$), $Z = 2$, monoclinic, space group $P2_1/c$ (no. 14), $\lambda = 1.54178$ Å, $T =$

223 K, $\omega/2\theta$ scans, 1483 reflections collected ($-h$, $-k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 1338 independent ($R_{\text{int}} = 0.034$) and 1221 observed reflections $[I \geq 2\sigma(I)]$, 93 refined parameters, $R = 0.041$, $wR^2 = 0.108$, max. residual electron density 0.40 (−0.50) e Å^{-3}, positional disorder at C1 refined with split positions to a ratio of 0.72 to 0.28, hydrogens calculated and refined as riding atoms.

*X-ray crystal structure analysis of **2b***

Formula $C_{14}H_{14}O_4$, $M = 246.3$, colourless crystal $0.35 \times 0.25 \times 0.02$ mm, $a = 25.335(15)$, $b = 5.697(3)$, $c = 8.505(2)$ Å, $\beta = 101.16(3)$, $V = 1204.3(10)$ Å^3, $\rho_{\text{calc}} = 1.358$ g cm^{-3}, $\mu = 8.25$ cm^{-1}, empirical absorption correction *via* ψ scan data ($0.761 \leq T \leq 0.984$), $Z = 4$, monoclinic, space group $C2/c$ (No. 15), $\lambda = 1.54178$ Å, $T = 223$ K, $\omega/2\theta$ scans, 1040 reflections collected ($\pm h$, $-k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.59$ Å^{-1}, 1015 independent ($R_{\text{int}} = 0.043$) and 499 observed reflections $[I \geq 2\sigma(I)]$, 84 refined parameters, $R = 0.048$, $wR^2 = 0.087$, max. residual electron density 0.15 (−0.17) e Å^{-3}, hydrogens calculated and refined as riding atoms, poorly diffracting crystal, probably twinned plates.

*Reaction of **2a** with titanium tetrachloride, preparation of **5a***

The neutral ligand precursor **2a** (0.50 g, 1.80 mmol) was dissolved in 10 ml of dichloromethane. Titanium tetrachloride (0.34 g, 1.80 mmol) was added slowly at room temperature *via* syringe. The reaction mixture turned orange immediately and the product began to precipitate as a bronze colored solid after a few minutes. After 2 h of stirring the solvent was removed *in vacuo* and the product collected as a bronze colored solid; yield of **5a**: 610 mg (86%). M. p. 300 °C. – IR (KBr): $\tilde{\nu} = 3052$ (m), 2960 (m), 1579 (m), 1455 (s), 1279 (s), 1240 (s), 1181 (w), 1161 (w), 1135 (m), 873 (s), 756 (s), 639 (s), 528 (s) cm^{-1}. – ^{1}H NMR (200 MHz, d$_8$-THF, 300 K): $\delta = 7.49$ (d, $^3J = 7.8$ Hz, 2H, 6-H), 7.39 (dd, $^3J = 7.8$ Hz, $^3J = 8.2$ Hz, 2H, 4-H), 7.01 (d, $^3J = 8.2$ Hz, 2H, 3-H), 6.93 (dd, $^3J = 7.8$ Hz, $^3J = 8.2$ Hz, 2H, 5-H), 3.12 (s, 4H, 7-H). – ^{13}C{^{1}H} NMR (50 MHz, d$_8$-THF, 300 K): $\delta = 158.5$ (C1), 134.0, 133.1, 125.0, 123.7 (C3 to C6), 116.5 (C2), 41.1 (C7). – $C_{14}H_{12}Cl_2O_2S_2Ti$ (395.2): calcd. C 42.55, H 3.06; found C 41.97, H 3.09.

*X-ray crystal structure analysis of **5a***

Single crystals were obtained from a dichloromethane solution at −30 °C. Formula $C_{14}H_{12}Cl_2O_2S_2Ti$, $M = 395.2$, red crystal $0.30 \times 0.07 \times 0.03$ mm, $a = 12.686(1)$, $b = 10.779(1)$, $c = 22.905(1)$ Å, $V = 3132.1(4)$ Å^3, $\rho_{\text{calc}} = 1.676$ g cm^{-3}, $\mu = 11.53$ cm^{-1}, empirical absorption correction via SORTAV ($0.724 \leq T \leq 0.966$), $Z = 8$, orthorhombic, space group $Pbca$ (No. 61), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 7291 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.68$ Å^{-1}, 3961 independent ($R_{\text{int}} = 0.049$) and 2944 observed reflections $[I \geq 2\sigma(I)]$, 190 refined parameters, $R = 0.050$, $wR^2 = 0.073$, max. residual electron density 0.33 (−0.33) e Å^{-3}, hydrogens calculated and refined as riding atoms.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 197914, 197915, and 197916. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, CambridgeCB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk].

*Reaction of **2a** with zirconium tetrachloride, preparation of **5c***

Zirconium tetrachloride (0.42 g, 1.80 mmol) was suspended in 10 ml of dichloromethane. At room temperature the reagent **2a** (0.50 g, 1.80 mmol) was added in several portions with stirring. After 2 h solvent was removed from the then clear solution. The product was isolated as a yellow solid, yield of **5c**: 675 mg, 85%. IR (KBr): $\tilde{\nu} = 3058$ (m), 2967 (m), 1584 (s), 1473 (s), 1275 (s), 1229 (s), 1064 (m), 854 (s), 755 (s), 597 (s) cm^{-1}. – ^{1}H NMR (200 MHz, d$_8$-THF, 300 K): $\delta = 7.5-6.9$ (m, 4H, 3-H, 6-H), 6.8 – 6.5 (m, 4H, 4-H, 5-H), 3.12 (s, 4H, 7-H). – ^{13}C{^{1}H} NMR (50 MHz, d$_8$-THF, 300 K): $\delta = 156.2$ (C1), 135.0, 130.5, 120.0, 114.2 (C3 to C6), 116.5 (C2), 34.8 (C7). – $C_{14}H_{12}Cl_2O_2S_2Zr$ (438.5): calcd. C 38.35, H 2.76; found C 37.90, H 2.89.

*Deprotonation of **2b**, formation of **6***

The neutral ligand precursor **2b** (246 mg, 100 mmol) was dissolved in 10 ml of THF. At −78 °C 1.25 ml (200 mmol) of a 1.6 M solution of n-butyl lithium in n-hexane was added dropwise with stirring. The mixture was slowly warmed to room temperature. After 4 h reaction time the solvent was removed *in vacuo* to yield **6** as a colorless solid, yield 242 mg (94%). M. p. 165 °C. – IR (KBr): $\tilde{\nu} = 3027$ (m), 1596 (m), 1497 (s), 1458 (s), 1313 (s), 1254 (m), 1115 (m), 1050 (m), 918 (m), 852 (m), 747 (s), 595 (m), 457 (m), cm^{-1}. – ^{1}H NMR (200 MHz, d$_8$-THF, 300 K): $\delta = 6.82$ (m, 4H), 6.69 (m, 2H), 6.35 (m, 2H, C_6H_4), 4.18 (s, 4H, 7-H). – ^{13}C{^{1}H} NMR (50 MHz, d$_8$-THF, 300 K): $\delta = 159.9$ (C1), 149.5 (C2), 123.3, 121.2, 114.3, 113.7 (arom. *C*H), 68.5 (C7).

*Reaction of **6** with titanium tetrachloride, synthesis of complex **5b***

Titanium tetrachloride (95 mg, 0.50 mmol) was added dropwise at ambient temperature to a solution of **6** (129 mg, 0.50 mmol) in 10 ml of diethyl ether. The reaction was instantaneous. After 2 h of stirring the precipitated lithium chloride was removed by filtration. Solvent was removed from the clear filtrate *in vacuo* to yield 169 mg (93%) of **5b**. M. p. 189 °C (decomp. at 217 °C). – IR (KBr): $\tilde{\nu}$ = 3065 (w), 1585 (w), 1486 (s), 1466 (m), 1269 (s), 1203 (m), 1117 (m), 1071 (m), 1032 (m), 933 (m), 863 (m), 797 (m), 749 (s), 624 (m) cm^{-1}. – ^1H NMR (200 MHz, d-chloroform, 300 K): $\delta = 6.9-6.7$ (m, 8H, 3-H to 6-H), 4.39 (s, 2H, 7-H). – $^{13}C\{^1H\}$ NMR (50 MHz, d-chloroform, 300 K): δ = 161.0 (C1), 143.3 (C2), 121.8, 119.3, 114.4, 112.1 (C3 to C6), 67.2 (C7). – $C_{14}H_{12}Cl_2O_4Ti$ (363.1): calcd. C 46.32, H 3.33; found C 46.31, H 3.70.

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