

Titanium complexes with sulfur-linked  
bis(phenolate) ligands

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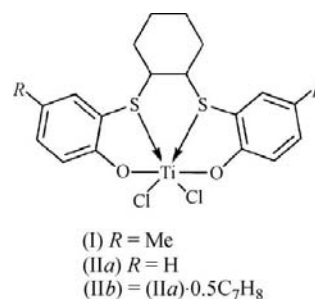
High-quality crystals of two bis(phenolate)titanium complexes, namely dichlorido{4,4'-dimethyl-2,2'-[cyclohexane-1,2-diylbis(sulfanediyl)]diphenolato}titanium(IV),  $[\text{Ti}(\text{C}_{20}\text{H}_{22}\text{O}_2\text{S}_2)\text{Cl}_2]$ , (I), and dichlorido{2,2'-[cyclohexane-1,2-diylbis(sulfanediyl)]diphenolato}titanium(IV),  $[\text{Ti}(\text{C}_{18}\text{H}_{18}\text{O}_2\text{S}_2)\text{Cl}_2]$ , (II), were obtained by reactive crystallization. Depending on the solvent, compound (II) was obtained as unsolvated (IIa) or as the toluene hemisolvate,  $[\text{Ti}(\text{C}_{18}\text{H}_{18}\text{O}_2\text{S}_2)\text{Cl}_2] \cdot 0.5\text{C}_7\text{H}_8$ , (IIb). These systems without bulky substituents on the aromatic phenolate rings serve as ideal model compounds for precatalysts. The excellent X-ray diffraction data will help clarify the nature of the mismatched interactions between the soft S atoms within the ligand and the hard titanium center. Molecule (I) has crystallographic  $C_2$  symmetry.

## Comment

Bis(phenolate) complexes of the early transition metals, such as titanium, are precatalysts for olefin polymerization. The ligand structure has a strong influence on the stereochemistry of the resulting polymer (Capacchione *et al.*, 2004; Beckerle *et al.*, 2007; Cohen *et al.*, 2007). For this reason, the bis(phenolate) ligands have been tuned by different substituents on the aromatic rings ( $R_1$  and  $R_2$ ) as well as by modifying the bridging unit. S atoms as part of the bridge can improve the catalytic activity, obviously as a result of hemilabile interactions between the soft donor S atom and the hard metal center (Froese *et al.*, 1999). In several S—C—S-bridged bis(phenolato)titanium complexes, the  $M \cdots S$  interactions lead to a stereorigid  $O,S,S',O'$ -tetradentate coordination in solution (Capacchione *et al.*, 2005). The nature of this so-called mismatched interaction is still not well understood and further details are not available from routine structure data. Ideal model compounds for structural studies should be as simple as possible, keeping the number of parameters low. Catalytically active systems usually contain bulky substituents such as *tert*-butyl groups in the *ortho* positions of the ring systems, which are often found to be disordered in the solid state. According to a previous structural comparison, the *ortho*

substituents in bis(phenolato)metal complexes barely influence the bond parameters around the metal center (Capacchione *et al.*, 2005).

Comparatively good results were obtained recently for a routine crystal structure determination of (I) (Meppelder *et al.*, 2008). We have now obtained high-quality crystals of this compound by reactive crystallization. In an analogous reaction, we have obtained crystals of a compound without the 4-methyl substituents, both without solvent in the crystal structure, (IIa), and as a toluene solvate, (IIb). Excellent diffraction results gave a resolution of  $\sin \theta/\lambda > 1.03$  for all of these examples and have led to good agreement factors even for the outstanding ratio of reflections to parameters. The molecular structures of the three compounds are shown in Figs. 1–3.



Although the structure model of (IIa) should be even more simple than that of (I), it only shows noncrystallographic  $C_2$  symmetry. As reported previously, (I) crystallizes on a crystallographic  $C_2$  axis. In addition in (IIb), solvent molecules are incorporated around inversion centers in the space group  $P2_1/n$ . The incorporated toluene solvent molecules are disordered in the crystal structure. There are no significant differences between the molecular structures. As in the parent molecule with a  $-\text{CH}_2\text{CH}_2-$  bridge (Snell *et al.*, 2003), the metal center adopts a distorted octahedral geometry, coordi-

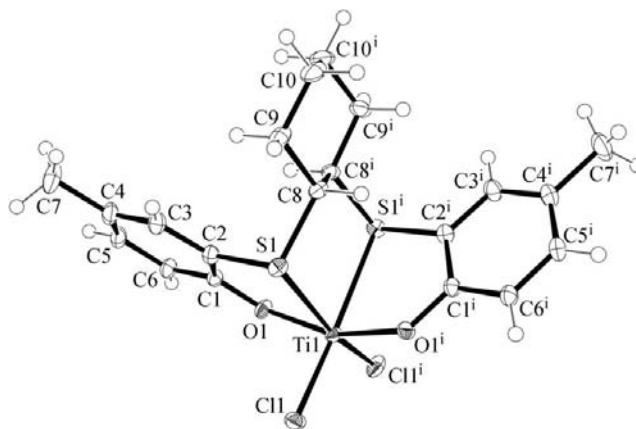
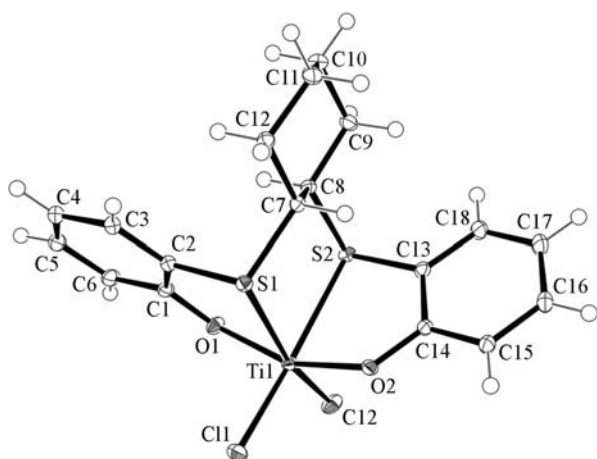


Figure 1

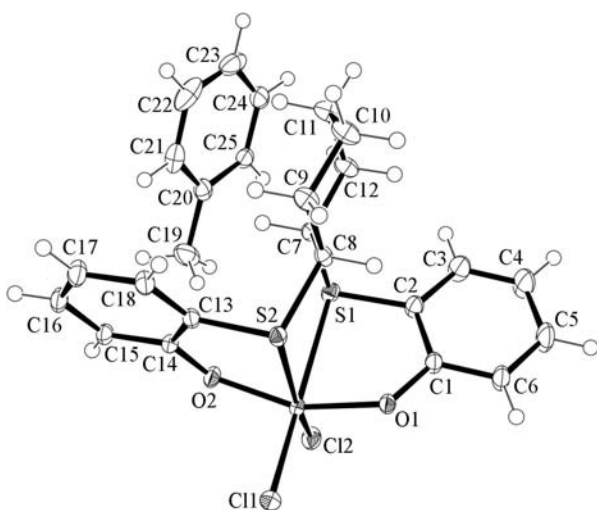
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i)  $-x + 1, -y, -z + \frac{1}{2}$ ]

nated by the two chloride ligands, both O-atom donors of the bis(phenolate) ligands and both S atoms. The Cl ligands and the S atoms are found in one plane. Both O atoms occupy pseudo-apical positions. The Ti—S distances are 2.6188 (2) Å in (I), 2.6141 (2) and 2.6270 (2) Å in (IIa), and 2.6031 (2) and 2.6261 (2) Å in (IIb), and are comparable to the Ti—S bond lengths in related compounds (range = 2.6–2.9 Å; Capacchione *et al.*, 2005). The stabilization of the helical configuration of the molecules by the relatively short Ti—S bond distances was noted previously. The overall geometry is chiral with a *gauche*-like conformation of the S—C—C—S bridge. The centrosymmetric packing arrangement contains both enantiomers.

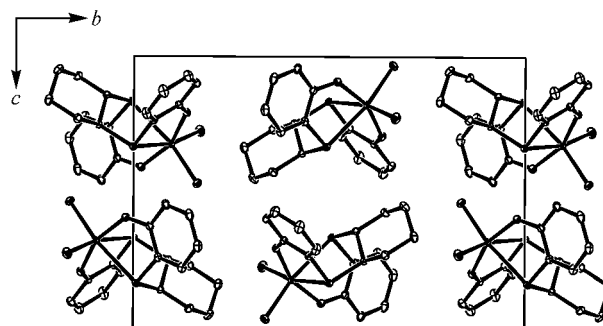
Packing diagrams (Figs. 4 and 5) show similarities between the arrangement of (IIa) and (IIb), which both crystallize in the space group  $P2_1/n$ . The projections along the crystallographic *a* axis show the positions of the toluene solvent



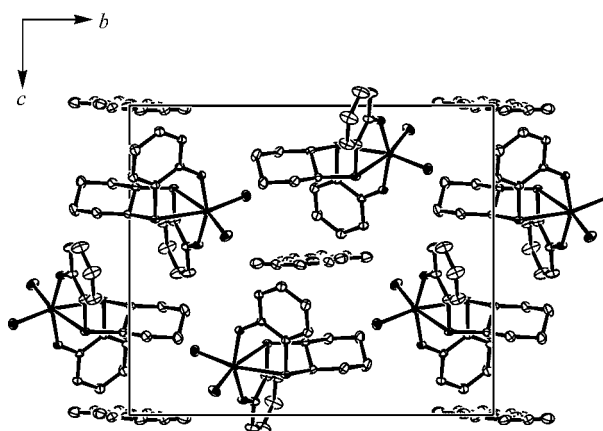
**Figure 2**  
The molecular structure of (IIa). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.



**Figure 3**  
The molecular structure of (IIb). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.



**Figure 4**  
The crystal packing of (IIa), viewed along the *a* axis. For the sake of clarity, H atoms have been omitted.



**Figure 5**  
The crystal packing of (IIb), viewed along the *a* axis. For the sake of clarity, H atoms have been omitted.

molecules. All three crystal structures exhibit close interatomic interactions involving the H atoms of the cyclohexyl fragment and the O atoms of neighboring bis(phenolate) ligands.

The close similarity of the molecular structure parameters underlines that (I) and (IIa) are suitable model compounds for bis(phenolato)metal-based precatalysts. We are currently working on the further interpretation of the diffraction data. By multipole refinement, we are now determining the electron density distribution in (I) and (IIa) to establish the nature of the interaction between the hard metal center and the soft S atom. These data will give further insight into the extent of  $O \cdots Ti \pi$  interaction in this class of compounds (Snell *et al.*, 2003).

## Experimental

Compound (I) was prepared as described previously (Meppelder *et al.*, 2008). High-quality crystals were obtained by reactive crystallization. A Schlenk tube containing  $TiCl_4$  (0.2 mmol) in toluene (2 ml) was covered with a layer of pure solvent (3 ml). A solution of 4,4'-dimethyl-2,2'-[cyclohexane-1,2-diylbis(sulfanediyl)]diphenol (0.2 mmol) in the same solvent (2 ml) was carefully added on top. Crystals formed within 3 d. The proligand 2,2'-[cyclohexane-1,2-diylbis(sulfanediyl)]diphenol was synthesized according to a literature procedure (Meppelder *et al.*, 2008) starting from *o*-mercaptophenol. Cyclohexene oxide (4.49 ml, 55 mmol) was added to

sodium 2-mercaptophenolate (50 mmol) in ethanol (50 ml) and the solution heated under reflux for 5 h. After removing the solvent under reduced pressure, the residue was dissolved in diethyl ether, washed with a saturated  $\text{NH}_4\text{Cl}$  solution and dried over  $\text{MgSO}_4$ . Evaporation of the solvent gave 10.704 g (47.7 mmol) of 2-(2-hydroxycyclohexylsulfanyl)phenol. This was dissolved in  $\text{CH}_2\text{Cl}_2$  (100 ml) and thionyl chloride (3.47 ml, 47.7 mmol) was added at 243 K. Removing the volatiles under reduced pressure left a residue, which was treated with  $\text{CH}_2\text{Cl}_2$ , washed with a solution of  $\text{NaHCO}_3$  and dried over  $\text{MgSO}_4$ . Evaporation of the solvent gave 10.143 g (41.8 mmol) of 2-(2-chlorocyclohexylsulfanyl)phenol as a brown oil. This was dissolved in  $\text{MeOH}$  and  $\text{CH}_2\text{Cl}_2$  and added to *o*-mercaptophenol (41.8 mmol). After refluxing for 3 h and removing the solvent *in vacuo*, a residue was obtained that was treated with  $\text{CH}_2\text{Cl}_2$  and filtered. Crystallization from ethanol and pentane (3:1 *v/v*) at 243 K gave 2,2'-[cyclohexane-1,2-diylbis(sulfanediy)]diphenol as colorless needles in a yield of 69% (9.53 g, 28.7 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.00–1.15 (*m*, 2H, CH of  $\text{C}_6\text{H}_{10}$ ), 1.23–1.41 ( $\text{CH}_2$  of  $\text{C}_6\text{H}_{10}$ ), 2.67 (*qd*, 2H,  $J = 9.7$  and 3.3 Hz, CH—S), 6.80 (*dt*, 2H,  $J = 7.6$  and 1.3 Hz, arom. CH), 6.96 (*dd*, 2H,  $J = 8.2$  and 1.1 Hz, arom. CH), 7.18 (*s*, 2H, OH), 7.24 (*ddd*, 2H,  $J = 8.1$ , 7.4 and 1.6 Hz, arom. CH), 7.39 (*dd*, 2H,  $J = 7.7$  and 1.5 Hz, arom. CH);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  25.5 (*s*, CH of  $\text{C}_6\text{H}_{10}$ ), 33.8 (*s*, CH of  $\text{C}_6\text{H}_{10}$ ), 52.3 (*s*, CH—S), 115.3 (*s*, arom. C), 115.8 (*s*, arom. C), 120.6 (*s*, arom. C), 131.8 (*s*, arom. C), 137.6 (*s*, arom. C), 158.1 (*s*, arom. C).

Compound (IIa) was prepared by reactive crystallization from  $\text{TiCl}_4$  (0.5 mmol) in benzene (2 ml) and 2,2'-[cyclohexane-1,2-diylbis(sulfanediy)]diphenol (0.5 mmol) in the same solvent (5 ml). Both solutions were separated by a layer of pure solvent (5 ml). Compound (IIb) was prepared analogously, except that toluene was used as solvent instead of benzene.  $^1\text{H}$  NMR (400 MHz, tetrahydrofuran-*d*<sub>8</sub>):  $\delta$  1.08–1.27 (*m*, 2H, CH of  $\text{C}_6\text{H}_{10}$ ), 1.29–1.43 (*m*, 2H, CH of  $\text{C}_6\text{H}_{10}$ ), 1.46–1.59 (*m*, 2H,  $\text{CH}_2$  of  $\text{C}_6\text{H}_{10}$ ), 1.95–2.07 (*m*, 2H,  $\text{CH}_2$  of  $\text{C}_6\text{H}_{10}$ ), 2.90–3.02 (*m*, 2H, S—CH), 6.59–6.68 (*m*, 2H, arom. CH), 6.73 (*dd*, 2H,  $J = 8.1$  and 1.2 Hz, arom. CH), 7.05 (*ddd*, 2H,  $J = 8.1$ , 7.3 and 1.7 Hz, arom. CH), 7.22 (*dd*, 2H,  $J = 7.7$  and 1.6 Hz, arom. CH);  $^{13}\text{C}$  NMR (100 MHz, tetrahydrofuran-*d*<sub>8</sub>):  $\delta$  23.8 (*s*, CH of  $\text{C}_6\text{H}_{10}$ ), 30.9 (*s*, CH of  $\text{C}_6\text{H}_{10}$ ), 50.4 (*s*, CH—S), 114.8 (*s*, arom. C), 115.1 (*s*, arom. C), 119.3 (*s*, arom. C), 129.6 (*s*, arom. C), 135.5 (*s*, arom. C), 157.9 (*s*, arom. C).

## Compound (I)

### Crystal data

$[\text{Ti}(\text{C}_{20}\text{H}_{22}\text{O}_2\text{S}_2)\text{Cl}_2]$	$V = 2159.34$ (7) $\text{\AA}^3$
$M_r = 477.30$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 10.7948$ (2) $\text{\AA}$	$\mu = 0.85$ $\text{mm}^{-1}$
$b = 10.9672$ (2) $\text{\AA}$	$T = 100$ K
$c = 18.5874$ (3) $\text{\AA}$	$0.29 \times 0.24 \times 0.15$ mm
$\beta = 101.1050$ (10) $^\circ$	

### Data collection

Bruker SMART CCD area-detector diffractometer	52551 measured reflections
Absorption correction: multi-scan (MULABS in PLATON; Spek, 2009)	10145 independent reflections
	7452 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.060$
$T_{\text{min}} = 0.791$ , $T_{\text{max}} = 0.883$	

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$	134 parameters
$wR(F^2) = 0.112$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{\text{max}} = 1.07$ $\text{e \AA}^{-3}$
10145 reflections	$\Delta\rho_{\text{min}} = -0.75$ $\text{e \AA}^{-3}$

## Compound (IIa)

### Crystal data

$[\text{Ti}(\text{C}_{18}\text{H}_{18}\text{O}_2\text{S}_2)\text{Cl}_2]$	$V = 1872.8$ (2) $\text{\AA}^3$
$M_r = 449.24$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 9.4627$ (7) $\text{\AA}$	$\mu = 0.98$ $\text{mm}^{-1}$
$b = 16.8985$ (4) $\text{\AA}$	$T = 100$ K
$c = 12.0810$ (11) $\text{\AA}$	$0.30 \times 0.22 \times 0.18$ mm
$\beta = 104.195$ (6) $^\circ$	

### Data collection

Bruker SMART CCD area-detector diffractometer	257682 measured reflections
Absorption correction: multi-scan (MULABS in PLATON; Spek, 2009)	28176 independent reflections
	22536 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.053$
$T_{\text{min}} = 0.759$ , $T_{\text{max}} = 0.844$	

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$	226 parameters
$wR(F^2) = 0.098$	H-atom parameters constrained
$S = 1.24$	$\Delta\rho_{\text{max}} = 0.84$ $\text{e \AA}^{-3}$
28176 reflections	$\Delta\rho_{\text{min}} = -0.73$ $\text{e \AA}^{-3}$

## Compound (IIb)

### Crystal data

$[\text{Ti}(\text{C}_{18}\text{H}_{18}\text{O}_2\text{S}_2)\text{Cl}_2] \cdot 0.5\text{C}_7\text{H}_8$	$V = 2227.60$ (11) $\text{\AA}^3$
$M_r = 445.31$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 9.7622$ (3) $\text{\AA}$	$\mu = 0.83$ $\text{mm}^{-1}$
$b = 16.3667$ (4) $\text{\AA}$	$T = 100$ K
$c = 14.5713$ (4) $\text{\AA}$	$0.36 \times 0.22 \times 0.10$ mm
$\beta = 106.8990$ (10) $^\circ$	

### Data collection

Bruker SMART CCD area-detector diffractometer	179195 measured reflections
Absorption correction: multi-scan (MULABS in PLATON; Spek, 2009)	20925 independent reflections
	13853 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.067$
$T_{\text{min}} = 0.755$ , $T_{\text{max}} = 0.922$	

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$	290 parameters
$wR(F^2) = 0.087$	H-atom parameters constrained
$S = 0.97$	$\Delta\rho_{\text{max}} = 0.73$ $\text{e \AA}^{-3}$
20925 reflections	$\Delta\rho_{\text{min}} = -0.47$ $\text{e \AA}^{-3}$

All H atoms were placed in idealized positions and allowed to ride on their parent atoms, with C—H distances of 0.95 (aromatic), 0.98 (methyl), 0.99 (cyclohexyl  $\text{CH}_2$ ) or 1.00  $\text{\AA}$  (cyclohexyl CH). For (IIa) and (IIb),  $U_{\text{iso}}(\text{H})$  values were set at  $1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{methyl C})$ . For (I), the isotropic displacement parameters were refined.

For all compounds, data collection: SMART (Bruker, 2003); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3350). Services for accessing these data are described at the back of the journal.

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