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Dichloro{N-[3-(η^5-cyclopentadienyl)-propyl]-4-toluenesulfonamido-κ^2N,O}-titanium(IV)

Cornelis Lensink, Graeme J. Gainsford* and Menno J. R. Brandsma

Industrial Research Limited, PO Box 31-310, Lower Hutt, New Zealand
Correspondence e-mail: g.gainsford@irl.cri.nz

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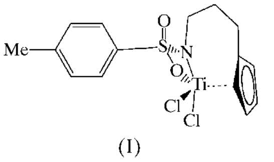
The title compound, [Ti($C_{15}H_{17}NO_2S$)Cl_2], has a Ti atom bound to the N and O atoms of a p-toluenesulfonamide ligand, which is tethered by a three-carbon chain to a η^5-cyclopentadienyl group. The distorted square-pyramidal geometry is completed by two Cl atoms. The Ti—N bond length of 2.0375 (13) Å is longer than that in related compounds, the N atom having asymmetric trigonal–planar geometry. Conformational strain relief is noted when compared with ethyl-tethered compounds.

Comment

Dichloro{N-[3-(η^5-cyclopentadienyl)propyl]-4-toluenesulfonamido-κ^2N,O}titanium(IV), (I), is related to previously reported structures (Lensink, 1998, hereinafter LENS; Lensink, Gainsford & Hosie, 2001; Lensink, Gainsford & Baxter, 2001, hereinafter LENS2). The racemic crystal structure consists of independent molecules (one enantiomer is shown in Fig. 1), with only weak intermolecular contacts, *e.g.* C3—H3···O2^i, with C3···O2 = 3.261 (2) Å [symmetry code: (i) $x, \frac{3}{2} - y, z - \frac{1}{2}$].



(I)

The Ti atom in (I) has a distorted square-pyramidal coordination and it is 0.820 (1) Å out of the mean plane through atoms N, O1, Cl1 and Cl2 [mean deviation 0.019 (1) Å] towards the cyclopentadienyl ring. In the related complexes [Ti($C_5H_4CH_2CH_2NSO_2C_6H_4CH_3$)$Cl_2$] (LENS) and [Ti($C_5H_4CH_2CH_2NSO_2C_6H_4CH_3$)($CF_3CO_3$)$_2$($C_4H_6O$)] (LENS2), which have an ethyl linkage from the N atom to the cyclopentadienyl ring, the Ti atoms have a distorted trigonal–bipyramidal geometry and distorted octahedral coordination, respectively. The longer ligand backbone (propyl) chain in (I) allows the complex to relieve some conformational strain by adopting a different geometry. Thus, the Ti—N—C8—C9, N—C8—C9—C15 and C9—C15—C10—C11 torsion angles of 57.4 (2), −62.3 (2) and 39.1 (2)°, respectively, are unstrained compared with the values of 27.3, −28.9 and 108.8° found in LENS.

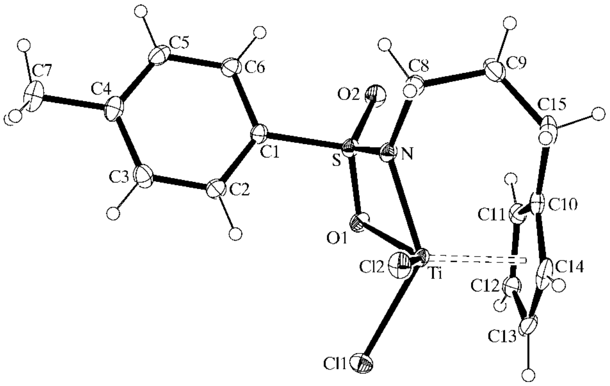


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

There is also a concomitant reduction in the displacement of the terminal C15 atom from the cyclopentadienyl plane, which is 0.031 (3) Å in (I) compared with 0.164 Å in LENS. The cyclopentadienyl ring planes [average out-of-plane deviation 0.005 (1) Å] and the Ti—Cg distance (2.023 Å) are identical to the data in LENS (Cg is the centre of gravity of the cyclopentadienyl ring). There are also no significant changes in the bond angles around the N atom in LENS and in (I). In contrast, the closely related four-coordinate Ti complexes studied by Sinnema *et al.* (1997), which (only) lack the sulfonamide O-atom coordination, show the reverse trend, with the propyl–cyclopentadienyl chain structure having more steric crowding than in the ethyl-linked molecule.

The N atom in (I) has an asymmetric trigonal–planar geometry, with the sum of the angles around it being 355.3°. The Ti—N distance of 2.0375 (13) Å is significantly longer (~0.17 Å) than the Ti—N distances in either [Ti(C_5H_5)(N^iPr_2)$_2Cl_2$] (Pupi *et al.*, 1995) or [Ti($C_5H_4CH_2CH_2N^iPr$)Cl_2] (Sinnema *et al.*, 1997), although it is within the wide ranges previously observed for Ti complexes (LENS2). The longer Ti—N distance suggests that this bond is best described as a single bond between the Ti and N atoms, consistent with the estimated Ti—N single-bond distance of 1.96–1.97 Å. The possible lone-pair interaction of atom O1 with the Ti atom perhaps diminishes the N($p\pi$)–M($d\pi$) interaction.

The Ti—O1 distance of 2.2008 (11) Å is much shorter than the sum of the van der Waals radii, and the difference in the S—O1 and S—O2 distances [1.491 (1) and 1.432 (1) Å, respectively] confirms that this is a single bond, as previously discussed in the LENS2 paper.

Experimental

A solution of $C_5H_5(CH_2)_3NHSO_2C_6H_4CH_3$ (0.60 g, 2.2 mmol) dissolved in toluene (5 ml) was added slowly to a Schlenk tube charged with Ti(NMe_2)$_4$ (0.50 g, 2.2 mmol) and toluene (15 ml) at

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room temperature. The reaction mixture was stirred overnight. After removal of the solvent *in vacuo*, a dark-orange oil remained, which was redissolved in toluene (15 ml). A solution of Me_3SiCl (0.81 g, 7.44 mmol) in toluene (5 ml) was then added slowly and the mixture stirred overnight. A dark-orange precipitate was isolated (yield 0.30 g, 0.77 mmol). Analysis calculated for $C_{15}H_{17}Cl_2NO_2STi$: C 45.7, H 4.4, N 3.6%; found: C 45.9, H 4.6, N 3.3%. Crystals of (I) were obtained from a solution in dichloromethane–pentane.

Crystal data

$[Ti(C_{15}H_{17}NO_2S)Cl_2]$
$M_r = 394.16$
Monoclinic, $P2_1/c$
$a = 16.986$ (3) Å
$b = 7.441$ (2) Å
$c = 13.488$ (5) Å
$\beta = 104.009$ (6)°
$V = 1654.1$ (8) Å^3
$Z = 4$

$D_x = 1.583$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3192 reflections
$\theta = 2.7$–25.8°
$\mu = 0.97$ mm^{-1}
$T = 153$ (2) K
Block, orange
0.88 × 0.66 × 0.50 mm

Data collection

Siemens SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.509$, $T_{max} = 0.615$
20 524 measured reflections

3386 independent reflections
3044 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 26.4°$
$h = -21 \rightarrow 21$
$k = -9 \rightarrow 9$
$l = -16 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.067$
$S = 1.06$
3386 reflections
200 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.039P)^2 + 0.611P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

All H atoms, except those on the methyl C7 atom, were constrained with $U_{iso}(H) = 1.2U_{eq}(C)$; the factor was 1.5 for the methyl H atoms. C—H distances were constrained in the range 0.95–0.99 Å.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996) and *SADABS* (Sheldrick, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

Table 1
Selected geometric parameters (Å, °).

Ti—N	2.0375 (13)	S—O2	1.4319 (12)
Ti—O1	2.2008 (11)	S—O1	1.4907 (12)
Ti—Cl2	2.2983 (7)	S—N	1.5765 (13)
Ti—Cl1	2.3087 (7)	S—C1	1.7608 (16)
N—Ti—O1	66.01 (5)	O2—S—N	116.34 (7)
O1—Ti—Cl2	134.67 (3)	C8—N—S	121.52 (11)
N—Ti—Cl1	132.78 (4)	C8—N—Ti	133.76 (10)
Cl2—Ti—Cl1	94.21 (3)	S—N—Ti	100.03 (7)

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1393). Services for accessing these data are described at the back of the journal.

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