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{(*E*)-5-[(4-Bromophenyl)diazenyl]-2-oxidobenzoato-κ^2O^1,O^2}bis(η^5-methylcyclopentadienyl)titanium(IV)

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Key indicators

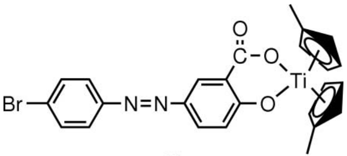
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.045
wR factor = 0.126
Data-to-parameter ratio = 12.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $[Ti(C_6H_7)_2(C_{13}H_7BrN_2O_3)]$, the Ti atom has a pseudo-tetrahedral coordination formed by two methylcyclopentadienyl ligands and a salicylate ligand. The salicylate acts as a bidentate ligand and coordinates to the metal centre *via* the hydroxy O atom and one carboxylate O atom.

Comment

Since 1954, when Cp_2TiCl_2 [dichlorobis(η^5-cyclopentadienyl)titanium] was first synthesized (Birmingham *et al.*, 1954), titanocene derivatives have attracted much attention. A number of titanocene derivatives have been synthesized and characterized; these exist in mononuclear (Radim *et al.*, 2004) and multinuclear (Aucott *et al.*, 2005) forms. However, reports on the structural characterization of substituted salicylate titanocenes are still scarce (Edwards *et al.*, 2001). We report here the crystal structure of the title compound, (I).



(I)

The title compound exhibits a pseudo-tetrahedral coordination geometry for the Ti atom, consisting of two methylcyclopentadienyl ligands and a salicylate ligand (Fig. 1). The salicylate ligand chelates, forming a six-membered ring. The Ti1—*Cg*1 and Ti1—*Cg*2 distances (*Cg*1 and *Cg*2 denote the centroids of the C14–C18 and C20–C24 rings, respectively) are 2.064 (2) and 2.066 (2) Å, respectively. The *Cg*1—Ti1—*Cg*2 and O1—Ti1—O3 angles are 132.40 (8) and 87.36 (10), respectively, and the *Cg*1/*Cg*2—Ti1—O1/O3 angles lie in the range 104.86 (9)–108.01 (9)°.

The molecules are linked into C18—H18···O2^{i} hydrogen-bonded chains along [110] [H18···O2^{i} = 2.44 Å and C18—H18···O2^{i} = 176°; symmetry code: (i) $-1 + x$, $1 + y$, z]. A Br1···Br1($2 - x$, $-2 - y$, $1 - z$) short contact of 3.417 (5) Å is observed in the crystal structure.

Experimental

Azosalicylic acid was prepared according to a literature method (Tushar *et al.*, 2001). $[\eta^5\text{-}(CH_3)C_5H_4]_2TiCl_2$ (2.0 mmol, 0.554 g) and acetylacetone (2.0 mmol) were dissolved in water (20 ml). The solution was added to a solution (50 ml) of azosalicylic acid (2.2 mmol, 0.71 g) dissolved in chloroform and diethyl ether (9:1). The mixture was stirred for about 30 min at room temperature, giving a deep-red

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solution. The solution was then separated, washed with saturated Na_2CO_3 and distilled water, and finally dried over anhydrous $MgSO_4$ and filtered. The filtrate was evaporated to dryness under vacuum. The solid product was recrystallized from a 2:3 mixture of dichloromethane and hexane. Crystals were allowed to grow at below room temperature. Single crystals suitable for X-ray diffraction were obtained after about two weeks. Analysis calculated for $C_{25}H_{21}BrN_2O_3Ti$: C 48.62, H 2.82%; found: C 11.73, H 2.75%.

Crystal data

$[Ti(C_6H_7)_2(C_{13}H_7BrN_2O_3)]$
$M_r = 525.25$
Triclinic, $P\overline{1}$
$a = 7.834$ (3) Å
$b = 7.922$ (3) Å
$c = 19.867$ (7) Å
$\alpha = 89.999$ (4)°
$\beta = 79.003$ (4)°
$\gamma = 68.763$ (4)°
$V = 1124.9$ (7) Å^3
$Z = 2$
$D_x = 1.551$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 2.19$ mm^{-1}
$T = 298$ (2) K
Plate, brown
0.48 × 0.45 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{\min} = 0.420$, $T_{\max} = 0.721$
5879 measured reflections
3892 independent reflections
2797 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.033$
$\theta_{\max} = 25.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.126$
$S = 1.02$
3892 reflections
321 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.063P)^2 + 0.039P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.45$ e Å^{-3}
$\Delta\rho_{\min} = -0.43$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.013 (2)

The Br atom is disordered over two sites and was modelled anisotropically, with site occupancies of 0.677 (13) and 0.323 (13). Both N atoms of the diazene group are disordered over two positions, with site occupancies of 0.781 (11) and 0.219 (11). The N—N and also the N—C distances involving the disordered atoms were restrained to be the same, and the U^{ij} components were restrained to approximately isotropic behaviour. All H atoms were placed in calculated positions and refined as riding, with C—H = 0.93–0.96 Å and $U_{\rm iso}$(H) = 1.2 or 1.5 times $U_{\rm eq}$(C).

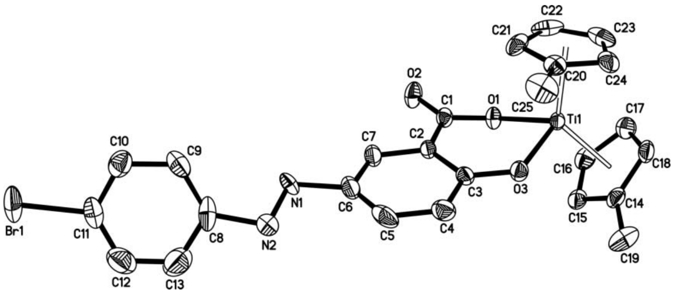

Figure 1
The molecular structure of (I), showing the atomic numbering. Displacement ellipsoids are drawn at the 30% probability level. H atoms and minor disorder components have been omitted.

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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References

Aucott, S. M., Kilian, P., Milton, H. L., Robertson, S. D., Slawin, A. M. Z. & Woollins, J. D. (2005). *Inorg. Chem.* **44**, 2710–2718.

Birmingham, J. M. & Wilkinson, G. (1954). *J. Am. Chem. Soc.* **76**, 4281–4284.

Bruker (2004). *SADABS* (Version 2.10), *SAINT* (Version 5.289) and *SMART* (Version 7.06a). Bruker AXS Inc., Madison, Wisconsin, USA.

Edwards, D. A., Mahon, M. F., Paget, T. J. & Summerhill, N. W. (2001). *Transition Met. Chem.* **26**, 116–119.

Radim, B., Ivana, C., Martin, P. & Ivan, P. (2004). *Appl. Organomet. Chem.* **18**, 262–263.

Sheldrick, G. M. (1997*a*). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (1997*b*). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Tushar, S. B. B., Sushmita, D., Simon, M. P., Edward, R. T. T., Eleonora, R., Ray, B. & Frank, E. S. (2001). *J. Organomet. Chem.* **633**, 7–17.