VU Research Portal

[2-8-(tert-Butylimino)-1-naphthyl]bis-(5-cyclopentadienyl)titanium(IV)

Kooijman, H.; van Leijen, M.; Akkerman, O.S.; Bickelhaupt, F.M.; Spek, A.L

published in

Acta Crystallographica Section E. Structure Reports
2006

DOI (link to publisher)

[10.1107/S1600536806021726](https://doi.org/10.1107/S1600536806021726)

document version

Publisher's PDF, also known as Version of record

[Link to publication in VU Research Portal](#)

citation for published version (APA)

Kooijman, H., van Leijen, M., Akkerman, O. S., Bickelhaupt, F. M., & Spek, A. L. (2006). [2-8-(tert-Butylimino)-1-naphthyl]bis-(5-cyclopentadienyl)titanium(IV). *Acta Crystallographica Section E. Structure Reports*, 62, 1545.
<https://doi.org/10.1107/S1600536806021726>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal ?

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

E-mail address:

vuresearchportal.ub@vu.nl

$[\eta^2\text{-}8\text{-(}tert\text{-Butylimino)-}1\text{-naphthyl]bis}(\eta^5\text{-cyclopentadienyl)titanium(IV)$

Huub Kooijman,^{a*} Monique M. van Leijen,^b Otto S. Akkerman,^b Friedrich Bickelhaupt^b and Anthony L. Spek^a

^aBijvoet Centre for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands, and ^bScheikundig Laboratorium, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

Correspondence e-mail: h.kooijman@chem.uu.nl

Key indicators

Single-crystal X-ray study

$T = 298\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$

R factor = 0.056

wR factor = 0.131

Data-to-parameter ratio = 18.4

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

The title compound, $[\text{Ti}(\text{C}_5\text{H}_5)_2(\text{C}_{15}\text{H}_{15}\text{N})]$, displays an iminoacyl fragment in an N-outside conformation, indicating that the $\text{C}=\text{N}$ vector points away from the σ -bonded C atom. Considering only the geometrical centres of all η -coordinated groups, the Ti^{IV} ion adopts a severely distorted tetrahedral configuration. The crystal packing displays a short $\text{C}-\text{H}\cdots\pi$ contact linking the molecules into an infinite chain running along the b -axis direction.

Comment

The structure of the title compound, (I), was determined in the course of our investigations on the synthesis and reactivity of small metallacycles. A similar compound has been reported by Campora *et al.* (1995) and a related compound with Zr by Berg & Petersen (1989).

The structure of (I) is shown in Fig. 1, and selected bond lengths and angles are listed in Table 1. The title compound has two η^5 -coordinated cyclopentadienyl (Cp) rings coordinated to the Ti^{IV} ion. The distances between the perpendicular projection of the Ti^{IV} ion on the Cp rings and their ring centroids (ring slippage) are 0.043 and 0.017 $\text{\AA}$ for the rings containing C16 and C21, respectively. The title compound further displays an iminoacyl fragment in an N-outside conformation, indicating that the $\text{C}=\text{N}$ vector points away from the σ -bonded atom C2 (Tatsumi *et al.*, 1985). When the Cp rings and the $\text{C}=\text{N}$ group are represented by their geometrical centres, as is suggested in Fig. 1, the Ti^{IV} ion displays a severely distorted tetrahedral configuration, with $X-\text{Ti}-Y$ angles in the range $88.24(11)$ – $133.16(9)^\circ$ (Table 3). In an alternative description, the Ti^{IV} ion takes part in two adjacent titanacycles, the three-membered ring Ti1/C11/N11 and the five-membered ring Ti1/C2/C1/C10/C11 . The maximum deviation from the least-squares plane through this last ring system is 0.028 (3) $\text{\AA}$ for C2. The $\text{Ti1}-\text{C2}$ bond is elongated by 0.2 $\text{\AA}$ compared with its parent compound 1,8-naphthalenediyltitanocene (Tinga *et al.*, 1994). The crystal packing displays a short $\text{C}-\text{H}\cdots\pi$ contact (Fig. 2 and Table 2),

Received 7 June 2006

Accepted 8 June 2006

Figure 1
A view of the title compound, showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

Figure 2
Section of the crystal packing illustrating the C4—H4... π interactions, viewed approximately perpendicular to the (102) planes. H atoms, with the exception of H4, have been omitted.

which links the molecules into an infinite chain running along the *b*-axis direction.

Experimental

A solution of 1,8-naphthalenediyltitanocene (0.1 mmol), prepared according to Tinga *et al.* (1994), in pentane (10 ml) was added to a solution of CN-*t*Bu (0.2 mmol) in toluene (2 ml) at room temperature. After stirring for 3 h, the solvents were evaporated and the residue was extracted with cyclopentane. Brown crystals were obtained after

a week from a solution in cyclopentane, which was kept at 280 K. Spectroscopic analysis: ^1H NMR (200 MHz, room temperature, C_6D_6 , reference $\text{C}_6\text{D}_5\text{H}$ = 7.17 p.p.m., p.p.m.): δ 7.85 (*m*, 1 H, H3), 7.83 (*m*, 1 H, H9), 7.68 (*m*, 1 H, H5), 7.58 (*m*, 1 H, H4), 7.50 (*m*, 1 H, H7), 7.37 (*m*, 1 H, H8), 5.20 (*s*, 10 H, 2Cp), 1.21 (*s*, 9 H, *t*Bu) (at 240 K a similar proton NMR spectrum was measured in CD_2Cl_2); ^{13}C NMR (50.3 MHz, room temperature, C_6D_6 , reference C_6D_6 = 128.0 p.p.m., p.p.m.): δ 220.2 (*d*, 3J = 3.3 Hz, C11), 191.2 (*m*, C2), 158.1 (*m*, C10), 140.3 (*ddd*, 1J = 154.1 Hz, 2J = 1.2 Hz, 3J = 7.5 Hz, C3), 137.3 (*d*, 3J = 7.6 Hz, C1 or C6), 135.0 (*dd*, 3J = 8.0/6.6 Hz, C6 or C1), 132.0 (*d*, 1J = 164.0 Hz, C9), 126.9 (*dd*, 1J = 150.9 Hz, 2J = 2.3 Hz, C4), 124.3 (*dd*, 1J = 158.4 Hz, 2J = 1.9 Hz, C8), 121.6 (*dd*, 1J = 157.3 Hz, 3J = 8.9 Hz, C7), 121.1 (*ddd*, 1J = 157.3 Hz, 3J = 9.4/8.2 Hz, C5), 105.5 (*dm*, 1J = 171.0 Hz, 2Cp), 59.2 (*d*, 2J = 4.2 Hz, C12), 29.3 (qsept, 1J = 125.4 Hz, 3J = 4.7 Hz, *t*Bu); IR (hexane) $\bar{\nu}$ (cm^{-1}) 1726 (*s*); HRMS (EI) calculated for $\text{C}_{21}\text{H}_{16}\text{N}^{48}\text{Ti}$: 330.0764; found: 330.076; MS (EI) *m/z* (relative intensities): 387 (not observed, M^+), 330 (77, [$M - \text{tBu}$] $^+$), 303 (17, [$M - \text{CHN-tBu}$] $^+$), 178 (38, Cp_2Ti^+), 128 (100, naphthalene, impurity).

Crystal data

$[\text{Ti}(\text{C}_5\text{H}_5)_2(\text{C}_{15}\text{H}_{15}\text{N})]$
 M_r = 387.33
Monoclinic, $P2_1/c$
 a = 15.0891 (12) Å
 b = 8.4475 (12) Å
 c = 15.6025 (18) Å
 β = 94.200 (13)°
 V = 1983.4 (4) Å³

Z = 4
 D_x = 1.297 Mg m^{-3}
Mo $K\alpha$ radiation
 μ = 0.44 mm^{-1}
 T = 298 K
Block, brown
0.5 × 0.4 × 0.2 mm

Data collection

Enraf-Nonius CAD-4
diffractometer
 $\omega/2\theta$ scans
Absorption correction: none
5661 measured reflections
4533 independent reflections

2344 reflections with $I > 2\sigma(I)$
 R_{int} = 0.200
 θ_{max} = 27.5°
3 standard reflections
frequency: 60 min
intensity decay: 1.5%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.056
 $wR(F^2)$ = 0.131
 S = 1.00
4533 reflections
247 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0508P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.28 \text{ e Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.28 \text{ e Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Ti1—N11	2.197 (3)	Ti1—C11	2.043 (3)
Ti1—C2	2.292 (3)	N11—C11	1.238 (4)
N11—Ti1—C2	104.45 (11)	C11—N11—C12	132.5 (3)
N11—Ti1—C11	33.70 (12)	N11—C11—C10	150.8 (3)
C2—Ti1—C11	70.75 (12)		

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C4—H4...Cg4 ⁱ	0.93	2.98	3.768 (5)	143

Symmetry code: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$. Cg4 is the centroid of the C1/C6/C7/C8/C9/C10 ring.

Table 3

Tetrahedral geometry of Ti1 (angles in °).

Cg1 represents the centroid of the Cp ring C16–C20; Cg2 represents the centroid of the Cp ring C21–C25; Cg3 represents the mid-point of the N=C bond.

C2–Ti1–Cg1	103.22 (10)
C2–Ti1–Cg2	101.46 (11)
C2–Ti1–Cg3	88.24 (11)
Cg1–Ti1–Cg2	133.16 (9)
Cg1–Ti1–Cg3	110.35 (9)
Cg2–Ti1–Cg3	109.60 (10)

H atoms were introduced in calculated positions, with C–H = 0.93 and 0.96 Å, and refined as riding on their carrier atoms, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{methyl C})$ or $1.2U_{\text{eq}}(\text{other C})$. The methyl groups were refined as rigid groups, allowing for rotation around the C–C bond.

Data collection: locally modified *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *SET4* (de Boer & Duisenberg, 1984); data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine struc-

ture: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

This work was supported in part (ALS) by the Council for the Chemical Sciences of the Netherlands Organization for Scientific Research (CW-NWO).

References

- Berg, F. J. & Petersen, J. L. (1989). *Organometallics*, **8**, 2461–2470.
- Boer, J. L. de & Duisenberg, A. J. M. (1984). *Acta Cryst.* **A40**, C-410.
- Campora, J., Buchwald, S. L., Gutierrez-Puebla, E. & Monge, A. (1995). *Organometallics*, **14**, 2039–2046.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5. Enraf–Nonius, Delft, The Netherlands.
- Sheldrick, G. M. (1985). *SHELXS86*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (1997). *HELENA*. Utrecht University, The Netherlands.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Tatsumi, K., Nakamura, A., Hofmann, P., Staufert, P., & Hoffman, R., (1985). *J. Am. Chem. Soc.* **107**, 4440–4451.
- Tinga, M. A. G. M., Schat, G., Akkerman, O. S., Bickelhaupt, F., Smeets, W. J. J. & Spek, A. L. (1994). *Chem. Ber.* **127**, 1851–1856.