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Key indicators

Single-crystal X-ray study
T = 298 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>.

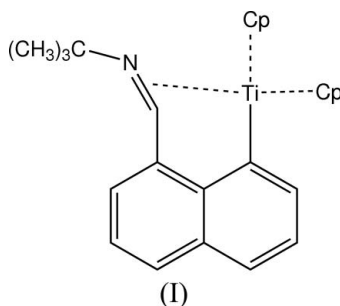
$[\eta^2\text{-}8\text{-(tert-Butylimino)-}1\text{-naphthyl]bis(\eta^5\text{-cyclopentadienyl)titanium(IV)}$

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.

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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 Å 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) Å for C2. The Ti1–C2 bond is elongated by 0.2 Å 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),

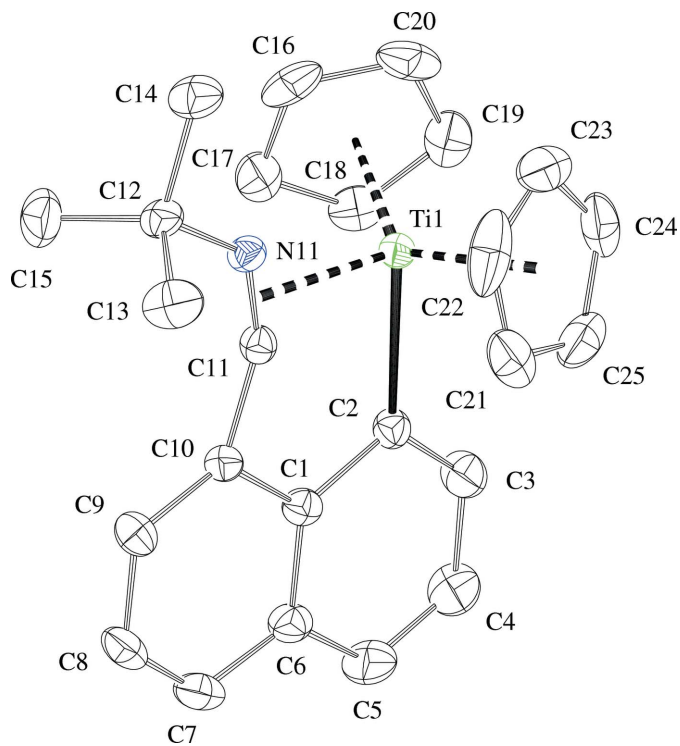


Figure 1
A view of the title compound, showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

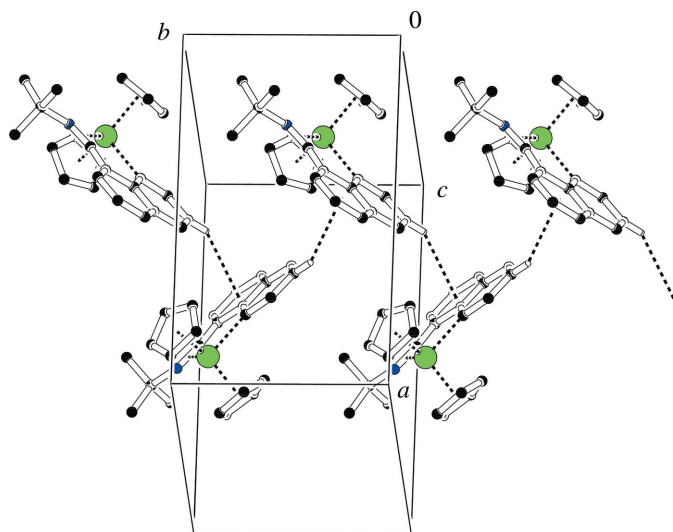


Figure 2
Section of the crystal packing illustrating the C4—H4... π interactions, viewed approximately perpendicular to the (10 $\bar{2}$) planes. H atoms, with the exception of H4, have been omitted.

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⁻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, C₆D₆, reference C₆D₅H = 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, ^tBu) (at 240 K a similar proton NMR spectrum was measured in CD₂Cl₂); ¹³C NMR (50.3 MHz, room temperature, C₆D₆, reference C₆D₆ = 128.0 p.p.m., p.p.m.): δ 220.2 (*d*, ³*J* = 3.3 Hz, C11), 191.2 (*m*, C2), 158.1 (*m*, C10), 140.3 (*ddd*, ¹*J* = 154.1 Hz, ²*J* = 1.2 Hz, ³*J* = 7.5 Hz, C3), 137.3 (*d*, ³*J* = 7.6 Hz, C1 or C6), 135.0 (*dd*, ³*J* = 8.0/6.6 Hz, C6 or C1), 132.0 (*d*, ¹*J* = 164.0 Hz, C9), 126.9 (*dd*, ¹*J* = 150.9 Hz; ²*J* = 2.3 Hz, C4), 124.3 (*dd*, ¹*J* = 158.4 Hz, ²*J* = 1.9 Hz, C8), 121.6 (*dd*, ¹*J* = 157.3 Hz, ³*J* = 8.9 Hz, C7), 121.1 (*ddd*, ¹*J* = 157.3 Hz, ³*J* = 9.4/8.2 Hz, C5), 105.5 (*dm*, ¹*J* = 171.0 Hz, 2Cp), 59.2 (*d*, ²*J* = 4.2 Hz, C12), 29.3 (*qsept*, ¹*J* = 125.4 Hz, ³*J* = 4.7 Hz, ^tBu); IR (hexane) $\bar{\nu}$ (cm⁻¹) 1726 (*s*); HRMS (EI) calculated for C₂₁H₁₆N⁴⁸Ti: 330.0764; found: 330.076; MS (EI) *m/z* (relative intensities): 387 (not observed, *M*⁺), 330 (77, [*M* - ^tBu]⁺), 303 (17, [*M* - CHN-^tBu]⁺), 178 (38, Cp₂Ti⁺), 128 (100, naphthalene, impurity).

Crystal data

[Ti(C₅H₅)₂(C₁₅H₁₅N)]
M_r = 387.33
Monoclinic, *P*2₁/*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*α 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* > 2σ(*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 > 2σ(*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 $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} < 0.001
 $\Delta\rho$ _{max} = 0.28 e Å⁻³
 $\Delta\rho$ _{min} = -0.28 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*.

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