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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>.

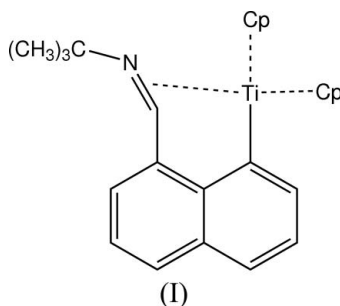
$[\eta^2\text{-}8\text{-(tert-Butylimino)-}1\text{-naphthyl]bis(\eta^5\text{-cyclopentadienyl)titanium(IV)}$

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

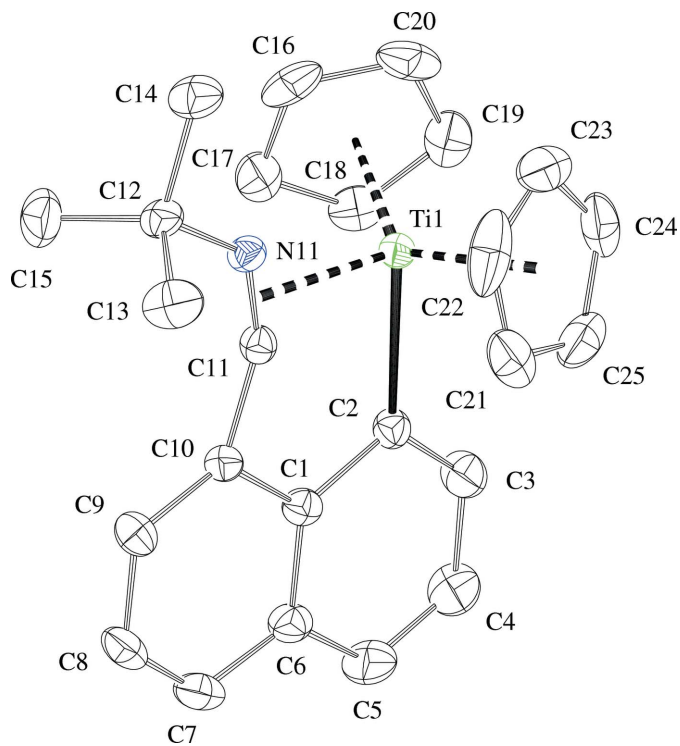


Figure 1
A view of the title compound, showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

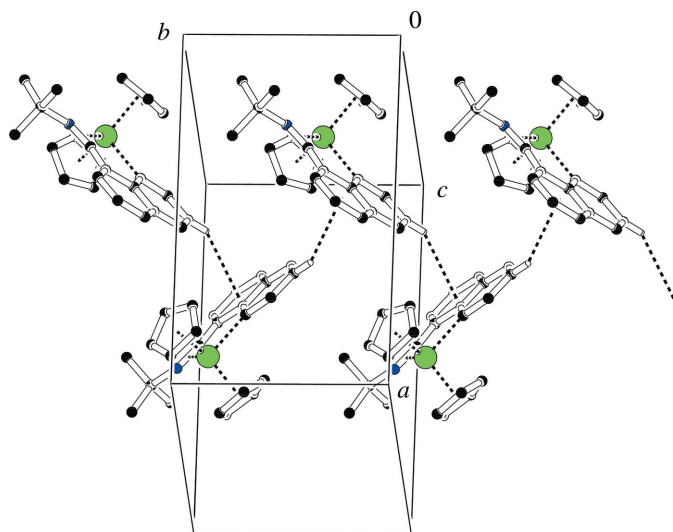


Figure 2
Section of the crystal packing illustrating the C4–H4... π interactions, viewed approximately perpendicular to the (10 $\bar{2}$) planes. H atoms, with the exception of H4, have been omitted.

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, P2₁/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 Kα 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
ω/2θ 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 F²
R[F² > 2σ(F²)] = 0.056
wR(F²) = 0.131
S = 1.00
4533 reflections
247 parameters

H-atom parameters constrained
w = 1/[σ²(F_o²) + (0.0508P)²]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.28 e Å⁻³
Δρ_{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, °).

D–H...A	D–H	H...A	D...A	D–H...A
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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