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THE CRYSTAL STRUCTURE OF A PHENYLIMINOMETHYLDICYCLOPENTADIENYLTITANIUM(III) COMPLEX, Cp_2Ti-η^2-C_6H_5CN-2,6-$(CH_3)_2C_6H_3$

F. van BOLHUIS,

Laboratorium voor Chemische Fysica, Rijksuniversiteit Groningen, Nijenborgh 16, 9747 AG Groningen (The Netherlands)

E.J.M. de BOER and J.H. TEUBEN *

Laboratorium voor Anorganische Chemie, Rijksuniversiteit Groningen, Nijenborgh 16, 9747 AG Groningen (The Netherlands)

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Summary

The crystal structure of $Cp_2TiC_6H_5CN$-2,6-$(CH_3)_2C_6H_3$ is reported. The iminoacyl ligand is η^2-coordinated at the metal (Ti—C 2.096(4), Ti—N 2.149(4) Å). The cyclopentadienyl ligands show the normal bent Cp_2Ti structure.

Introduction

Reaction of Cp_2TiR with isonitriles, R′NC yields either adducts, $Cp_2TiR \cdot R'NC$, or insertion products, $Cp_2TiC(R)$=NR′, depending on the nature of R and R′ [1]. The high thermal stability and low reactivity of these insertion products, e.g. towards two-electron donor ligands such as N_2, CO or RCN, are unusual for normal Cp_2TiR derivatives, and suggest a high coordinative saturation of the metal. This could be achieved by η^2-coordination of the iminoacyl ligand, but spectroscopic evidence in favour of this bonding was not convincing. Determination of the structure of $Cp_2TiC_6H_5CN$-2,6-$(CH_3)_2C_6H_3$ (I) by X-ray diffraction was undertaken in order to ascertain the exact coordination mode of the RC=NR′ ligand.

Results

Description of the structure. The structure of the molecule is shown schematically in Fig. 1a. The bond lengths and angles are listed in Table 1 and Fig. 1b; best least squares planes and dihedral angles are given in Table 2. The most

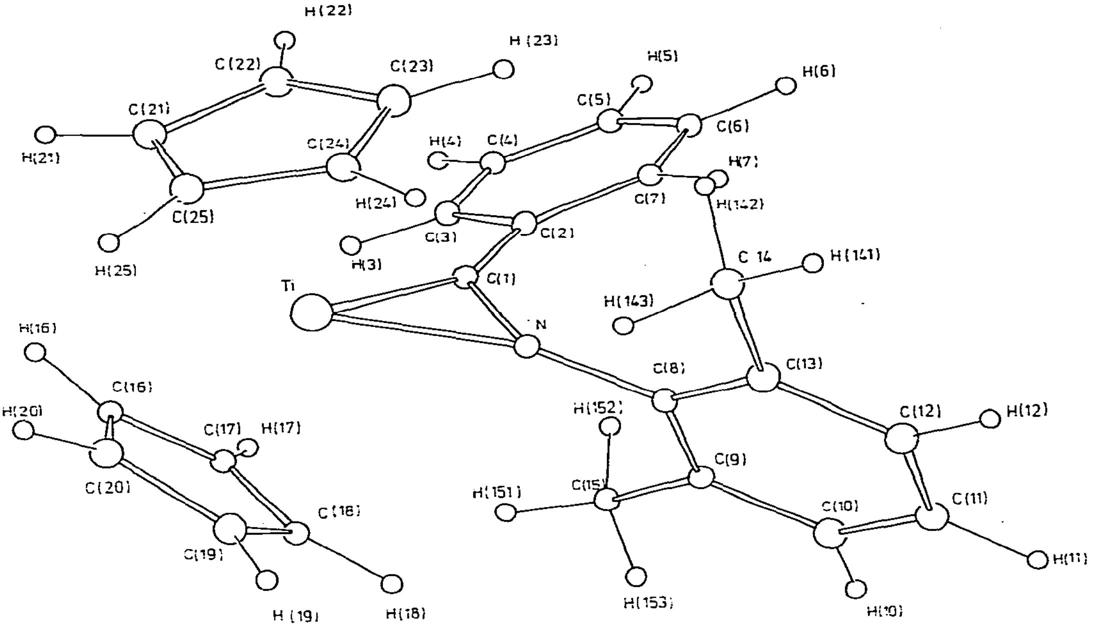

Fig. 1a. Schematical view of $Cp_2Ti\text{-}\eta^2\text{-}C_6H_5CN\text{-}2,6\text{-}(CH_3)_2C_6H_3$.

interesting feature of the structure is the η^2-coordination of the iminoacyl ligand.

Fig. 1 and Table 1 show that the cyclopentadienyl rings are planar and η^5-coordinated to the titanium atom; they are essentially staggered. The distances of the titanium atom to the centroids of the two rings (*RC*I and *RC*II) are

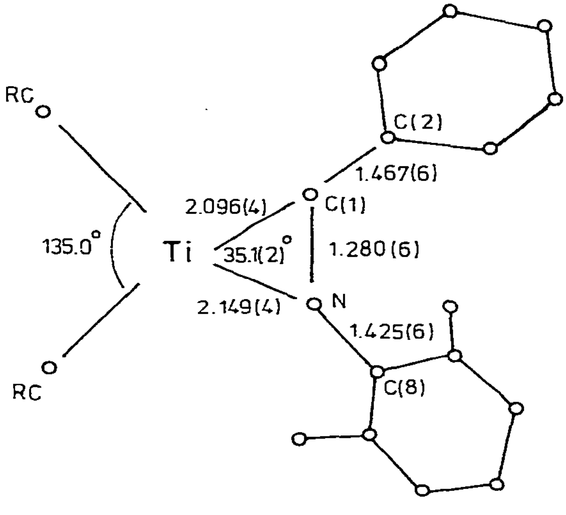

Fig. 1b. Skeletal view of $Cp_2Ti\text{-}\eta^2\text{-}C_6H_5CN\text{-}2,6\text{-}(CH_3)_2C_6H_3$.

TABLE 1

BOND LENGTHS [a] AND ANGLES

The hydrogen atoms are numbered according to the carbon atom to which they are attached.

	(Å)		(°)
Ti—C(1)	2.096(4)	N—Ti—C(1)	35.1(2)
Ti—N	2.149(4)	Ti—N—C(1)	70.2(3) (γ_1)
Ti—C(16)	2.356(11)	C(1)—N—C(8)	130.6(3) (β_1)
Ti—C(17)	2.370(9)	Ti—C(1)—C(2)	157.4(4) (α_2)
Ti—C(18)	2.392(7)	Ti—C(1)—N	74.7(2) (γ_2)
Ti—C(19)	2.383(8)	N—C(1)—C(2)	127.4(4) (β_2)
Ti—C(20)	2.377(6)	C(3)—C(2)—C(7)	118.4(4)
Ti—C(21)	2.383(6)	C(3)—C(2)—C(1)	118.0(4)
Ti—C(22)	2.389(6)	C(7)—C(2)—C(1)	123.4(5)
Ti—C(23)	2.386(6)	C(2)—C(3)—C(4)	119.8(6)
Ti—C(24)	2.380(7)	C(3)—C(4)—C(5)	120.5(6)
Ti—C(25)	2.363(6)	C(4)—C(5)—C(6)	120.2(5)
N—C(1)	1.280(6)	C(5)—C(6)—C(7)	119.5(6)
N—C(8)	1.425(6)	C(6)—C(7)—C(2)	121.6(6)
C(1)—C(2)	1.467(6)	N—C(8)—C(9)	120.9(5)
C(2)—C(3)	1.396(8)	N—C(8)—C(13)	118.6(4)
C(2)—C(7)	1.372(7)	C(8)—C(9)—C(10)	121.4(6)
C(3)—C(4)	1.396(8)	C(9)—C(10)—C(11)	118.0(6)
C(4)—C(5)	1.359(10)	C(10)—C(11)—C(12)	119.6(7)
C(5)—C(6)	1.380(10)	C(11)—C(12)—C(13)	121.8(7)
C(6)—C(7)	1.383(7)	C(8)—C(9)—C(15)	122.9(5)
C(8)—C(9)	1.409(7)	C(15)—C(9)—C(10)	119.1(5)
C(8)—C(13)	1.412(8)	C(12)—C(13)—C(14)	120.3(6)
C(9)—C(10)	1.410(9)	C(8)—C(13)—C(14)	120.9(5)
C(10)—C(11)	1.378(11)	Ti—N—C(8)	158.7(3) (α_1)
C(11)—C(12)	1.377(10)		
C(12)—C(13)	1.382(9)		
C(9)—C(15)	1.520(9)		
H(143)—H(24)	2.27		
H(142)—H(23)	2.24		
H(151)—H(18)	2.11		
C(16)—C(17)	1.385(12)	C(17)—C(16)—C(20)	108.0(8)
C(17)—C(18)	1.385(12)	C(16)—C(17)—C(18)	107.6(7)
C(18)—C(19)	1.385(10)	C(17)—C(18)—C(19)	108.7(6)
C(19)—C(20)	1.392(12)	C(18)—C(19)—C(20)	107.9(7)
C(16)—C(20)	1.349(14)	C(19)—C(20)—C(16)	108.4(7)
RCI—Ti [b]	2.069		
C(21)—C(22)	1.415(8)	C(24)—C(25)—C(21)	108.3(5)
C(21)—C(25)	1.404(10)	C(25)—C(21)—C(22)	107.2(6)
C(22)—C(23)	1.384(10)	C(21)—C(22)—C(23)	107.3(6)
C(23)—C(24)	1.385(8)	C(22)—C(23)—C(24)	109.3(5)
C(24)—C(25)	1.386(10)	C(23)—C(24)—C(25)	108.0(6)
*RC*II—Ti [b]	2.062		
		*RC*I—Ti—*RC*II	135.0

[a] Standard deviations in parentheses are in units of the last decimal place. [b] *RC*I = C(16)—C(20) ring centroid; *RC*II = (C(21)—C(22) ring centroid.

2.069 Å and 2.062 Å. The dihedral angle between the ring planes is 46.3° (Table 2) and the *RC*I—Ti—*RC*II angle is 135.0° (Table 1). The Ti—*RC* lines are not exactly perpendicular to the respective planes, as has been observed for other compounds Cp_2TiR_n [2].

The iminoacyl ligand is coordinated via the carbon and nitrogen atom at the titanium atom. The Ti—C(1) bond length of 2.096(4) Å is similar to Ti—C dis-

TABLE 2. LEAST-SQUARES PLANES [a]

(a) Equations of the planes

Atoms	Plane	*P*	*Q*	*R*	*S*
C(16)—C(20)	I	−0.4009	−0.5767	0.7118	4.8031
C(21)—C(25)	II	0.4995	0.8662	0.0132	8.3867
C(2)—C(1)—N—C(8)	III	−0.6664	−0.6472	0.3701	−3.2777
C(8)—C(15)	IV	0.2781	−0.5784	0.7669	8.2876
C(2)—C(7)	V	0.3019	0.9443	0.1312	5.2496
Ti—C(1)—N	VI	−0.6256	−0.6813	0.3802	−2.9087
*R*CI—Ti—*R*CII	VII	0.8659	−0.4963	0.0630	7.1096

(b) Distances of some atoms from the respective planes (in Å)

Atoms	Plane I	Atoms	Plane II	Atoms	Plane III
C(16)	−0.006	C(21)	0.006	C(2)	−0.014
C(17)	0.000	C(22)	−0.007	C(1)	0.033
C(18)	0.005	C(23)	0.005	N	−0.035
C(19)	−0.009	C(24)	−0.001	C(8)	0.015
C(20)	0.009	C(25)	−0.003	Ti	−0.017
				C(5)	−0.134
				C(11)	0.111

Atoms	Plane IV	Atoms	Plane V
C(8)	−0.001	C(2)	−0.012
C(9)	−0.006	C(3)	0.014
C(10)	0.006	C(4)	−0.006
C(11)	0.002	C(5)	−0.005
C(12)	−0.008	C(6)	0.007
C(13)	0.008	C(7)	0.001
C(14)	−0.007	C(1)	0.068
C(15)	−0.031		
N	0.082		

(c) Angles (°)

I—II	46.3
III—IV	61.8
III—V	40.2
VI—VII	79.6
(C(1)—N)—VII	76.4

[a] The equations of the planes are $PI + QJ + RK = S$ in orthogonal Ångstrom space where *P*, *Q* and *R* are direction cosines, referred to orhtogonal unit axes *I*, *J* and *K*, with $I \parallel a$, $J \parallel b$ and $K \parallel c$ *.

tances observed in the compounds $Cp_2Ti(Cl)$-η^2-$COCH_3$ (2.07 Å) [4], $[Cp_2Ti(Ph_2C_2O)]_2$ (2.099 Å) [5] and $(Cp_2Ti)_2C_4Ph_2$ (2.083 Å) [3] which also have *dihapto* coordination of the ligand. The bonds in these compounds are rather short compared with the Ti—C bonds in η^1-complexes Cp_2TiR_n [2,3]. The Ti—N bond length of 2.149(4) Å is significantly shorter than that in the amino complexes $Cp_2Ti[2\text{-}(CH_3)_2NCH_2C_6H_4]$ (2.46(2) Å) [2] and $CpTi[2\text{-}(CH_3)_2NCH_2C_6H_4]_2$ (2.389(4) Å) [6] but longer than that in the dinitrogen complex $[Cp_2Ti\text{-}p\text{-}CH_3C_6H_4]_2N_2$ (1.962(6) Å) [7] and the diazido complex $Cp_2Ti(N_3)_2$ (2.03(1) Å) [8].

The C(1)—N bond length is 1.280(6) Å, comparable with that in other η^1-

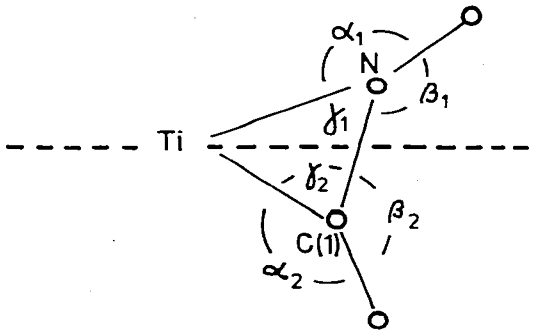

Fig. 2. Geometry and angles in the Ti—C(1)—N-plane.

and η^2-complexes (see Table 3). The *R*CI—Ti—*R*CII plane does not go through the centre of C(1)—N, N lying closer to the plane than to C(1) (distances 0.406 and 0.841 Å, respectively). The dihedral angle between the Ti—C(1)—N and *R*CI-Ti-*R*CII plane is 79.6° and the C(1)-N angle with the *R*CI-Ti-*R*CII plane is 76.4°. The iminoacylgroup C(2)—C(1)—N—C(8) is almost planar and Ti lies close to the average plane (Table 2). The phenyl and xylyl rings are bent away from the metal with angles β_1 and β_2 of 130.6(3)° and 127.4(4)°, respectively; other angles associated with the iminoacyl group are α_1 158.7(3)°, α_2 157.4(4)°, γ_1 70.2(3)°, γ_2 74.7(2)° and C(1)—Ti—N 35.1(2)° (Fig. 2).

The phenyl and xylyl rings are twisted out of the C(2)—C(1)—N—C(8) plane in order to decrease their mutual repulsion, as would be expected for a *cis*-conformation of an iminoacyl ligand. (For *trans*-iminoacyls a similar twisting of the aryl rings is observed and attributed to steric effects [9].) These twist angles are limited by the cyclopentadienyl ligands; the calculated distances between some of the methyl protons of the xylyl group and cyclopentadienyl protons are short (H(143)—H(24) 2.27 Å, H(142)—H(23) 2.24 Å, H(151)—H(18) 2.11 Å; sum of the Van der Waals radii 2.4 Å).

It appears that the molecule Cp_2Ti-η^2-C_6H_5CN-2,6-$(CH_3)_2C_6H_3$ is fairly crowded except for a hole on the front side of the molecule between the cyclopentadienyl and xylyl rings (see Fig. 1a).

Discussion

The structure of compound I unequivocally shows the η^2-coordination of the iminoacyl ligand at the titanium atom. This ligand can be regarded formally as a three-electron donor ligand, as it was recently shown to be in iminoacylmolybdenum(II) complexes [10] and a ruthenium(II) compound [11]. From a comparison of η^1- and η^2-iminoacylmolybdenum(II) compounds Adams and Chodosh suggest that η^2-coordination results in an increase of the acetylenic character of the CN bond. This is reflected in an increase of the angles N—C(1)—C(2) (β_2) and C(1)—N—C(8) (β_1) (Table 3, Fig. 2). For the η^2-ruthenium(II) complex the angles β_1 and β_2 (Table 3) are also larger than would be expected for a η^1-iminoacyl ligand. In our compound the angles β_1 and β_2 are again increased, but less than in the other η^2-complexes (Table 3).

A consequence of the increase of the angles β_1 and β_2 is a shift of ν(CN) in

TABLE 3

BOND ANGLES β_1 AND β_2, ν(CN) AND C=N BOND LENGTHS IN SOME IMINOACYL COMPLEXES

Complex	β_1(°) [a]	β_2(°) [a]	ν(CN) (cm^{-1})	d(C=N) (Å)	Ref.
$Ru(\eta^2$-p-$CH_3C_6H_4CN$-p-$CH_3C_6H_4)Cl(CO)(PPh_3)_2$	139.6(5)	137.6(5)	1654	1.30(1)	11
$CpMo(CO)_2$-η^2-$CH_3CNC_6H_5$	138.9(4)	134.7(5)	1670	1.233(6)	10
Cp_2Ti-η^2-C_6H_5CN-2,6-$(CH_3)_2C_6H_3$	130.6(3)	127.3(4)	1575	1.280(6)	this work
$(\mu$-$H)Os_3(CO)_{10}(\mu$-$C_6H_5CNCH_3)$	125.1(7)	120.2(7)	— [b]	1.278(10)	12
$CpMo(CO)[P(OCH_3)_3]$-η^1-$CH_3CNC_6H_5$	124.3(9)	119.4(9)	1570	1.266(12)	10
trans-$PtI(\eta^1$-CH_3CN-p-$ClC_6H_4)[P(C_2H_5)_3]_2$	125.4(10)	115.4(10)	~1580	1.287(13)	13

[a] Referred to Fig. 2. [b] Not reported.

the IR spectrum to higher wavenumbers. From the literature data on η^1- and η^2-iminoacyl ligands, it is tempting to suggest a relationship between ν(CN) and the mode of coordination of the ligand. In η^2-complexes ν(CN) is observed at high values (>1650 cm^{-1}) [10.11], about 80—100 cm^{-1} higher than in the corresponding η^1-complexes.

In the titanium(III) complex under discussion the crystal structure leaves no doubt about the η^2-coordination of the ligand, but the angles β_1 and β_2 are only slightly increased. The ν(CN) is observed at 1573 cm^{-1} which means that it falls within the range by η^1-complexes. An explanation for this discrepancy may be found in the afore-mentioned steric repulsion between the aryl rings and the cyclopentadienyl groups that prevents β_1 and β_2 to increase further. Apparently the increase in these angles is not enough to shift ν(CN) from the η^1-range into the η^2-range.

In addition to this effect there may also be an electronic effect, viz. back bonding of the unpaired electron at titanium into the antibonding CN-orbitals. This would cause the ν(CN) to shift to lower wavenumbers. These arguments illustrate that more information is needed before a reliable empirical rule for assigning the coordination mode based on IR can be given.

In the molecular orbital scheme for Cp_2M systems as given by Lauher and Hoffmann [14] the unpaired electron in Cp_2Ti-η^2-RC=NR′ (formally trivalent titanium with a d^1 configuration) will occupy the $1a_1$ orbital, while the $2a_1$ and b_2 orbitals are involved in the bond with the iminoacyl ligand (assuming C_{2v} symmetry). The occupation of the $1a_1$ orbital by the unpaired electron in Cp_2-Ti-η^2-RC=NR′ explains its inertness towards two-electron donor ligands such as N_2, CO or RCN while one-electron donors X (X = I, SC_6H_5) yield the compounds $Cp_2Ti(X)RCNR'$. In the IR spectrum of the latter compounds ν(CN) is observed at about 1660 cm^{-1}, and the iminoacyl carbon atom resonance in the ^{13}C NMR spectra shows a downfield shift to about 215—230 ppm [1]. Both features are in line with literature data and strongly indicate that in these compounds the iminoacyl ligand is still η^2-coordinated.

TABLE 4

CRYSTALLOGRAPHIC DATA AND DETAILS OF EXPERIMENTAL METHODS

Data	Experimental details
Monoclinic Space group $P2_1/c$	Weissenberg photographs of zero and higher layer lines.
a 14.370(15) Å b 7.804(5) Å c 18.459(10) Å β 105.44(6)° Z 4	Least squares refinement based on $\sin^2\theta$ values of 25 reflections from counter data; $\lambda(\text{Cu-}K_\alpha)$ 1.5418 Å
D_{calc} = 1.29 gcm^{-3} μ(Cu) = 38.1 cm^{-1}	Dimensions of crystal: 0.6 × 0.15 × 0.3 mm^3
3999 intensities	Automatic Nonius CAD-4 extended counterarm diffractometer, Ni-filtered Cu-radiation; ω-scan, $\sin\theta/\lambda \leqslant 0.6226$ Å^{-1}. Reflections with I(net) $\leqslant$ 0 were discarded.
3160 independent $\lvert F(hkl)\rvert$ values with $\lvert F\rvert > 3\sigma(\lvert F\rvert)$	Corrections for L.P. factors; no absorption corrections.

TABLE 5

FINAL PARAMETERS [a]

(a) Coordinates for the non-hydrogen atoms

(b) Parameters U_{ij} (in 10^{-2} Å^2) of the temperature factor $\exp[-2\pi^2(h^2(a^*)^2U_{11} + ... + 2ha^*kb^*U_{12} ...)]$ of the non-hydrogen atoms

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{13}$	$2U_{23}$
Ti	0.80489(6)	0.27420(12)	0.58800(4)	4.06(6)	5.32(7)	3.39(5)	0.1(1)	1.7(1)	0.2(1)
N	0.7691(3)	0.1402(6)	0.4825(2)	3.9(2)	6.5(3)	3.6(2)	−0.1(4)	2.3(3)	−0.7(4)
C(1)	0.7038(3)	0.2512(6)	0.4831(2)	4.4(2)	4.9(3)	4.3(2)	0.2(4)	2.9(4)	0.3(4)
C(2)	0.6204(3)	0.2971(7)	0.4209(2)	4.3(3)	6.0(3)	4.3(2)	−0.1(5)	1.3(4)	0.0(4)
C(3)	0.5358(4)	0.3484(9)	0.4383(3)	5.2(3)	10.0(5)	5.8(3)	2.9(6)	3.3(5)	0.2(6)
C(4)	0.4561(4)	0.3997(10)	0.3810(4)	4.5(3)	12.6(6)	8.2(4)	4.6(7)	1.5(6)	0.8(8)
C(5)	0.4610(5)	0.4049(9)	0.3085(4)	6.4(4)	10.3(5)	6.7(4)	3.8(8)	−2.9(6)	2.6(7)
C(6)	0.5449(5)	0.3585(9)	0.2908(3)	7.8(4)	11.0(5)	4.5(3)	5.4(8)	0.5(6)	−0.6(6)
C(7)	0.6235(4)	0.3043(8)	0.3472(3)	5.9(3)	7.7(4)	4.4(3)	2.6(6)	1.9(5)	0.5(5)
C(8)	0.7743(3)	0.0137(7)	0.4281(2)	4.8(3)	6.6(3)	3.5(2)	1.3(5)	1.6(4)	−0.3(4)
C(9)	0.7016(4)	−0.1114(7)	0.4057(3)	6.2(3)	6.5(4)	4.7(3)	1.9(6)	1.2(5)	0.2(5)
C(10)	0.7141(5)	−0.2394(8)	0.3552(3)	9.8(5)	6.4(4)	5.6(3)	1.0(7)	−0.4(6)	−1.1(6)
C(11)	0.7945(6)	−0.2423(10)	0.3279(3)	11.0(6)	8.5(5)	5.7(4)	7.0(9)	3.6(7)	−0.8(7)
C(12)	0.8642(5)	−0.1179(9)	0.3501(3)	8.3(4)	9.4(5)	5.3(3)	6.3(8)	4.8(6)	−0.5(7)
C(13)	0.8568(4)	0.0094(8)	0.4003(3)	6.0(3)	7.9(4)	4.7(3)	3.3(6)	3.4(5)	0.4(5)
C(14)	0.9339(4)	0.1428(9)	0.4230(4)	5.5(3)	11.0(6)	9.2(5)	0.0(7)	7.5(7)	0.7(8)
C(15)	0.6114(4)	−0.1142(8)	0.4339(4)	6.0(4)	7.9(5)	8.7(4)	−2.8(7)	2.4(6)	−0.6(7)
C(16)	0.7422(8)	0.2357(11)	0.6925(5)	16.4(9)	8.4(6)	9.5(5)	4.9(12)	18.7(12)	2.0(9)
C(17)	0.6946(5)	0.1198(13)	0.6385(5)	5.5(4)	14.2(8)	10.9(6)	0.2(9)	6.7(8)	13.5(11)
C(18)	0.7620(6)	0.0014(9)	0.6286(3)	11.7(6)	6.4(4)	5.9(4)	−3.9(8)	5.4(8)	2.0(6)
C(19)	0.8487(5)	0.0438(11)	0.6752(4)	7.4(4)	10.9(6)	7.4(4)	4.6(8)	5.6(7)	7.9(8)
C(20)	0.8357(7)	0.1882(12)	0.7157(3)	12.2(7)	12.7(7)	3.8(3)	−8.5(12)	1.7(7)	1.7(7)
C(21)	0.8432(5)	0.5556(8)	0.6370(3)	12.4(6)	5.9(4)	6.9(4)	−3.9(8)	5.7(8)	−3.3(6)
C(22)	0.8017(5)	0.5727(8)	0.5588(3)	8.2(4)	5.4(4)	8.2(4)	−0.1(7)	4.0(7)	1.3(6)
C(23)	0.8639(4)	0.4956(8)	0.5229(3)	7.8(4)	6.5(4)	5.7(3)	−4.0(7)	3.5(6)	1.8(6)
C(24)	0.9425(4)	0.4298(8)	0.5762(4)	5.7(3)	6.8(4)	8.8(4)	−4.4(6)	2.4(6)	2.2(7)
C(25)	0.9300(5)	0.4649(8)	0.6466(4)	9.3(5)	7.5(4)	6.9(4)	−7.5(8)	−3.3(7)	1.3(7)

[a] Standard deviations (in units of the last decimal place) are given in parentheses.

Experimental

The compound Cp_2Ti-η^2-C_6H_5CN-2,6-$(CH_3)_2C_6H_3$ (I) was prepared as described previously [1]. Crystals of I were grown by careful crystallization from n-pentane. Most of the crystals were deformed and only after several attempts was a suitable crystal found. Because of the air sensitivity of the compound, crystals were sealed in capillaries and mounted with Vaseline; no density determination by floatation methods was possible.

The structure was solved by direct methods making use of the program Multan [15] of the X-ray 1976 system of Crystallographic Programs [16]. An E-map, based on the signs with the best combined figure of merit revealed the positions of the titanium atom and of 14 of the non-hydrogen atoms. From a difference map calculated after a few cycles of isotropic least-squares refinement of these atoms, the remaining non-hydrogen atoms were found. After further anisotropic least-squares refinement of all parameters a difference map was calculated in which hydrogen atoms linked to the ring atoms and one hydrogen of each methyl group were observed clearly. The remaining hydrogen atoms of the methyl groups were found from geometrical considerations. A few maxima in the difference map around the Ti atom (peak heights approximately 0.6 e $Å^{-3}$) are thought to be due to a neglect of absorption correction [17]. In the later stages of the refinement the H atoms were fixed at 1.08 Å from the corresponding C atom, without changing the observed C—H directions; only the B(H) parameters of the isotropic temperature factor $\exp(-B \sin^2\theta/\lambda^2)$ were refined. All refinements were done with unit weights. Scattering factors were taken from ref. 18 for Ti, C and N and ref. 19 for H; anomalous dispersion was not taken into account. The final value of $R \equiv [\Sigma(\Delta F)^2/\Sigma(F_o)^2]^{1/2}$ was 0.074 based on 3160 reflections. Crystallographic data and experimental details are listed in Table 4.

The final coordinates and their standard deviations are listed in Table 5. A list of observed and calculated structure factors, H-parameters and *B*-factors are available from the authors on request.

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