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STRUCTURE OF 2-(DIMETHYLAMINOMETHYL)PHENYLDICYCLOPENTADIENYLTITANIUM(III)

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Summary

The crystal and molecular structure of the title compound have been determined by a single-crystal X-ray diffraction study. The structure consists of monomeric units. The titanium atom is pseudotetrahedrally coordinated by two η^5 -cyclopentadienyl groups, one carbon of the aryl ligand (Ti—C 2.22 Å) and a nitrogen atom of the dimethylamino group. The Ti—N distance of 2.46 Å is 0.3 Å shorter than the expected Van der Waals distance, which indicates a strong interaction between Ti and N.

Introduction

The observation that the compound $\text{Cp}_2\text{Ti}[2-\{(\text{CH}_3)_2\text{NCH}_2\}\text{C}_6\text{H}_4]$ (I) is thermally much more stable than the related compounds Cp_2TiR (II) in which R is an unsubstituted or *m*- or *p*-substituted aryl group, was explained by assuming internal coordination of the amino group to the metal atom [1]. Such occupation of the vacant reactive coordination site on the titanium atom effectively blocks low-activation-energy decomposition pathways (c.f. e.g. [2]). However, coordination of the amino function to the titanium atom could not be deduced unequivocally from the spectral and magnetic properties of the compound. Therefore an X-ray diffraction study was undertaken to determine the complete three-dimensional configuration of the molecule.

Results and discussion

The crystal structure consists of monomeric units $(\text{C}_5\text{H}_5)_2\text{Ti}[2-\{(\text{CH}_3)_2\text{NCH}_2\}\text{C}_6\text{H}_4]$. There are no distances shorter than the sum of the relevant Van der Waals radii between the individual molecules. A stereopicture of the molecule is shown in Fig. 1 and a more detailed view of the surroundings of Ti is given in Fig. 2. From these figures and from the bond lengths and angles in Table 1 we see that the Ti atom in (I) is pseudotetrahedrally coordinated. The coordinating

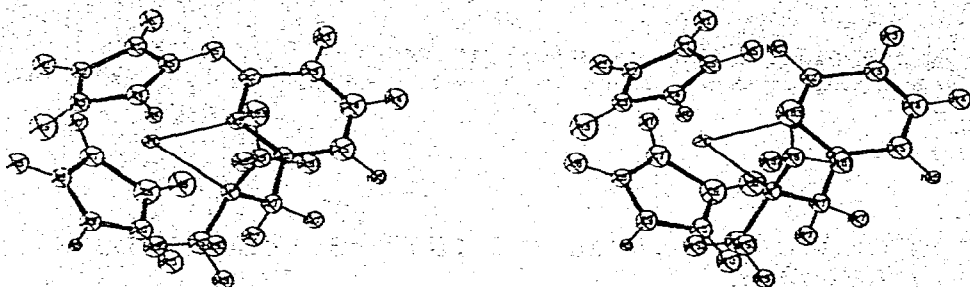


Fig. 1. Stereopicture of the $\text{Cp}_2\text{Ti}[2-\{(\text{CH}_3)_2\text{NCH}_2\}\text{C}_6\text{H}_4]$ molecule with numbering scheme.

ligands are the two η^5 -cyclopentadienyl groups, one carbon atom (C(11)) of the aryl group and the nitrogen atom of the $\text{N}(\text{CH}_3)_2$ group.

The Ti atom is closely surrounded by the four ligands. It is noteworthy that the distance Ti—N of 2.46 Å is some 0.3 Å shorter than the sum of the Van der Waals radii ($r(\text{Ti}) \approx 1.35$, $r(\text{N}) = 1.5$ Å), indicating a strong interaction between Ti and N. Although the Ti atom is coordinately not completely saturated (it is a 17 electron species) the close surrounding of the metal by the ligands may explain the inertness of the molecule with respect to thermal decomposition and to complexation with dinitrogen or ligands such as RCN [1,3]. In this respect the present Ti compound (I) differs from the related compounds (II) mentioned in the introduction, which readily undergo the above reactions because of the presence of a vacant and accessible coordination site.

Although the structure of (I) is not sufficiently accurate to permit a detailed comparison with bond lengths and angles in related compounds, some comments can be made. The conformation of the molecule shows signs of quite strong steric interactions between the ligands bonded to Ti. Comparison with less density packed Cp_2TiR_n compounds (Table 2) shows that in the Cp_2Ti moiety of (I) the (staggered) Cp rings are pushed away from the metal by the

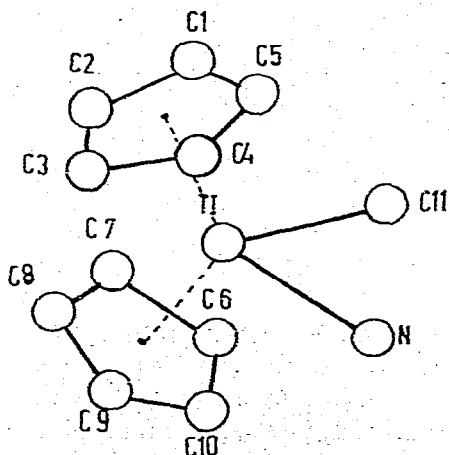


Fig. 2. The coordination around titanium.

TABLE 1
BOND LENGTHS AND ANGLES OF THE MOLECULE ^a

(a) Atomic distances in Å					
Ti—C(1)	2.40(3)	C(1)—C(2)	1.41(4)	C(11)—C(12)	1.42(3)
Ti—C(2)	2.40(3)	C(2)—C(3)	1.52(3)	C(12)—C(13)	1.47(5)
Ti—C(3)	2.45(3)	C(3)—C(4)	1.48(4)	C(13)—C(14)	1.22(5)
Ti—C(4)	2.44(3)	C(4)—C(5)	1.30(4)	C(14)—C(15)	1.32(5)
Ti—C(5)	2.37(3)	C(5)—C(1)	1.46(4)	C(15)—C(16)	1.34(5)
Ti—C(6)	2.45(5)	C(6)—C(7)	1.49(6)	C(16)—C(11)	1.39(3)
Ti—C(7)	2.33(3)	C(7)—C(8)	1.35(4)	C(16)—C(17)	1.57(3)
Ti—C(8)	2.36(3)	C(8)—C(9)	1.35(3)	C(17)—N	1.46(4)
Ti—C(9)	2.41(3)	C(9)—C(10)	1.33(5)	C(18)—N	1.51(3)
Ti—C(10)	2.47(4)	C(10)—C(6)	1.35(4)	C(19)—N	1.59(3)
Ti—C(11)	2.22(3)	Ti—RC(I) ^b	2.08		
Ti—N	2.46(2)	Ti—RC(II)	2.09		
(b) Bond angles (in degrees)					
C(11)—C(12)—C(13)	116(2)	C(15)—C(16)—C(17)	132(2)		
C(12)—C(13)—C(14)	126(3)	C(11)—C(16)—C(17)	114(2)		
C(13)—C(14)—C(15)	120(40)	C(16)—C(17)—N	112(2)		
C(14)—C(15)—C(16)	121(3)	Ti—C(11)—C(12)	127(2)		
C(15)—C(16)—C(11)	124(2)	Ti—C(11)—C(16)	118(2)		
C(16)—C(11)—C(12)	114(2)				
C(1)—C(2)—C(3)	110(2)	C(6)—C(7)—C(8)	109(2)		
C(2)—C(3)—C(4)	103(3)	C(7)—C(8)—C(9)	107(3)		
C(3)—C(4)—C(5)	109(3)	C(8)—C(9)—C(10)	110(3)		
C(4)—C(5)—C(1)	115(3)	C(9)—C(10)—C(6)	112(2)		
C(5)—C(1)—C(2)	104(2)	C(10)—C(6)—C(7)	102(2)		
C(11)—Ti—N	73(1)	C(17)—N—C(18)	107(2)		
C(11)—Ti—RC(I)	109	C(17)—N—C(19)	109(2)		
C(11)—Ti—RC(II)	107	C(17)—N—Ti	102(1)		
N—Ti—RC(I)	111	C(18)—N—Ti	113(1)		
N—Ti—RC(II)	109	C(19)—N—Ti	112(1)		
RC(I)—Ti—RC(II)	131	C(18)—N—C(19)	113(2)		
(c) Dihedral angles					
Ring I	Λ	TiC(11)N	26		
Ring II	Λ	TiC(11)N	27		

^a Atoms are numbered according to Fig. 1. Standard deviations in parentheses are in units of the last decimal place. ^b RC denotes Ring-Centroid.

TABLE 2
LENGTHS OF Ti—C(σ) BONDS (Å) AND GEOMETRY OF Cp₂Ti GROUPS IN SOME ORGANOMETALLIC COMPOUNDS

Compound	Ti—C(σ)	Ti—RC ^a	Ti—C(Cp)	RC(I)—Ti—RC(II)	Ref.
(I)	2.22	2.08	2.40	131°	Present work
Cp ₂ Ti— π (allyl)		2.06	2.40	132	[4]
[Cp ₂ TiC ₆ H ₄ CH ₃ p] ₂ N ₂	2.22	2.05	2.37	138	[5]
Cp ₂ Ti—2,6-xylyl	2.18	2.03	2.35	141	[6]
Cp ₂ TiR _n		2.05 ₅ ^b			[7]

^a RC = centroid Cp ring. ^b Average value for the 18 compounds given in Table 5 of ref. [7].

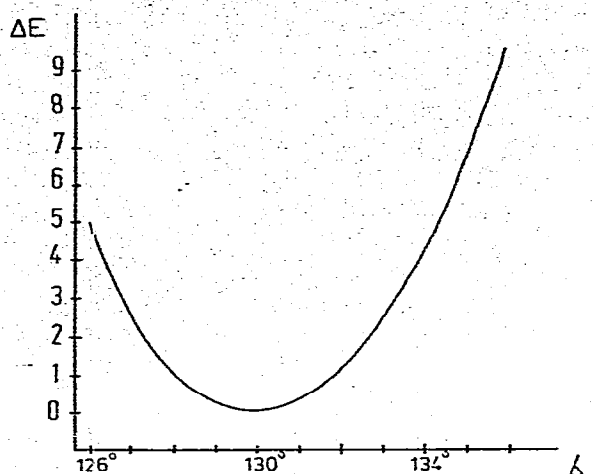


Fig. 3. Potential energy due to non-bonded interaction as a function of RC(I)—Ti—RC(II) (ϕ).

2-[(CH₃)₂NCH₂]C₆H₄ ligand. This results in large Ti—C(Cp) distances of about 2.40 Å, RC(I)—Ti distances of 2.08 and 2.09 Å and a RC(I)—Ti—RC(II) angle of 131°. That a value of 131° is sterically favorable for RC(I)—Ti—RC(II) was shown by calculation of the potential energy due to non-bonded interactions for different RC(I)—Ti—RC(II) values leaving the rest of the structure unchanged (c.f. the energy minimum at 130° in Fig. 3 and experimental). The conformation of the Ti[2-[(CH₃)₂NCH₂]C₆H₄] part of (I) also indicates significant steric effects. The angle N—Ti—C(11) of 73° shows good agreement with the corresponding angle of 73.4° in CpTi[2-[(CH₃)₂NCH₂]C₆H₄]₂ (III), showing the small bite of the bidentate ligand [8]. A similar situation occurs at the Sn atom in [2-(CH₃)₂NCH₂C₆H₄]Sn(C₆H₅)₂Br where the angle N—Sn—C is 75° [9].

In (I) the distances Ti—N of 2.46 Å and Ti—C(11) of 2.22 Å are larger than in (III), 2.389 and 2.197 Å respectively. That the length of the Ti—N bond seems to be especially sensitive to steric effects is also demonstrated by the Ti—N lengths observed in the 8-quinolinato and 2-methyl-8-quinolinato derivatives Ti(OR)₂L₂ (L = quinolinato). In the latter the Ti—N distance is considerably longer than that in the former (2.35 vs. 2.22 Å), apparently because of the methyl group *ortho* to the ligand N atom [10]. Further the large difference between the two independent Ti—N distances of 2.318 and 2.214 Å in TiCl₃ · 3 pyridine has been ascribed to steric effects [11].

Finally it is worthwhile to compare the aryl ligand [2-[(CH₃)₂NCH₂]C₆H₄] in (I) with the [(CH₃)₂C₆H₃] ligand in Cp₂Ti-2,6-xylyl (IV). In both compounds, apart from the Ti—C(σ) bond, there is a short distance between Ti and one of the atoms of the ligand, N in (I) and (methyl)H in (IV) [6]. Moreover in both compounds the C₆ ring of the ligand shows similar deviations from a regular hexagonal shape.

Experimental

Cp₂Ti[2-[(CH₃)₂NCH₂]C₆H₄] was synthesized by the method given in ref. [1]. Purple crystals were grown by sublimation at 110–120°C/0.1 mmHg. Be-

TABLE 3

CRYSTAL DATA AND EXPERIMENTAL DETAILS OF THE STRUCTURE DETERMINATION OF $\text{Cp}_2\text{Ti}[2\text{-}(\text{CH}_3)_2\text{NCH}_2]\text{C}_6\text{H}_4]$ AT 20°C

Monoclinic	Weissenberg photographs of zero and higher layer lines.
Space group $P2_1$	Observed optimized diffractometer angles θ , φ and χ of 5 reflections.
$a = 8.00(2)$, $b = 14.92(2)$, $c = 8.10(3)$ Å, $\beta = 112.5(2)^\circ$	$\lambda(\text{Mo-K}\alpha) = 0.7107$ Å.
$D_o = 1.3$ g cm $^{-3}$	Flotation method.
$Z = 4$, $D_x = 1.16$ g cm $^{-3}$	Automatic Nonius 4-circle diffractometer Zr filtered Mo-irradiation,
2044 reflections with $I(\text{nett}) > 0$	$\theta - 2\theta$ scan, $\sin \theta/\lambda < 0.70$ Å $^{-1}$.
1038 independent $ F(hkl) $ values $> 5\sigma(F)$	Corrections for Lorentz polarization; no absorption correction ($\mu = 4.9$ cm $^{-1}$, dimensions crystal 0.02–0.04 cm)

cause of the air sensitivity, the crystals were mounted in glass capillaries. Crystallographic data and details of the experimental work are listed in Table 3. During the data collection the intensities of the reference reflections were reduced to about 50% of their initial values, presumably because of decomposition of the crystal by small amounts of oxygen and/or moisture in the capillary. Because of these inaccuracies in the intensities the structure determination was not easy. The positions of the Ti atom and the two cyclopentadienyl carbon rings were found from an E map calculated with the best phase set obtained by MULTAN [12] for 377 reflections with $E > 1.3$. The remaining non-hydrogen atoms were located in successive cycles of least squares refinements and difference synthesis calculations by making use of the information from the difference maps and the Patterson synthesis.

In the least squares refinement anisotropic temperature factors were used for Ti and isotropic temperature factors for C and N. During the final cycles the hydrogen atoms were taken into account with fixed geometrically reasonable values for their positions and isotropic thermal parameters. We used the weighting scheme $w = [w_c^{-1} + 0.012|F|^2]^{-1}$, w_c being the weight based on counting statistics. The residuals $R = \Sigma|\Delta F|/\Sigma|F_o|$ and $R_w = [\Sigma w|\Delta F|^2/\Sigma w|F_o|^2]^{1/2}$ decreased to 0.14 and 0.18 respectively for the 1038 reflections considered in the refinement. The final parameters of the non-hydrogen atoms are given in Table 4. A list of observed and calculated structure factors is available on request. The computations were done on a Cyber 74-16 with the X-ray 1975 [13] system.

To check whether a value of 131° is sterically favorable for the angle RC(I)—Ti—RC(II) (φ) the potential energy due to non-bonded interactions was calculated as a function of φ with the program WMIN [14]. Equation 1 was applied for the non-bonded energy E_{ij}^{nb} between two atoms i and j .

$$E_{ij}^{\text{nb}} = (A_i + A_j) \exp[(A_i + A_j) - R_{ij}/(B_i + B_j)] - C_i C_j / R_{ij}^6 \quad (1)$$

with R_{ij} = distance between i and j . The constants A , B and C were taken from ref. [15] for carbon and hydrogen and from ref. [16] for nitrogen. The angle RC(I)—Ti—RC(II) was varied by rotating ring I and ring II by amounts of $+\frac{1}{2}\Delta\varphi$ and $-\frac{1}{2}\Delta\varphi$ around the normal through Ti unto the plane RC(I)—Ti—RC(II). Apart from this, the structure was kept unchanged. Fig. 3 shows that the energy has a minimum for $\varphi = 130^\circ$.

TABLE 4

COORDINATES AND TEMPERATURE PARAMETERS u^2 (in 10^{-2} \AA^2) OF THE NON-HYDROGEN ATOMS. STANDARD DEVIATIONS IN UNITS OF THE LAST DECIMAL PLACE ARE GIVEN IN PARENTHESES

Atom	x/a	y/b	z/c	u^2		
Ti	0.9616(5)	0.4190(2)	0.9260(4)			
C(1)	1.046(4)	0.356(2)	1.221(4)	5.9(7)		
C(2)	0.984(3)	0.444(2)	1.228(3)	4.7(6)		
C(3)	0.784(5)	0.451(3)	1.099(5)	4.4(5)		
C(4)	0.741(4)	0.359(2)	1.038(4)	5.9(7)		
C(5)	0.886(4)	0.309(2)	1.099(4)	5.1(7)		
C(6)	1.173(3)	0.501(2)	0.828(3)	8.4(10)		
C(7)	1.172(4)	0.535(2)	1.002(4)	6.7(8)		
C(8)	1.011(4)	0.575(2)	0.970(3)	4.9(6)		
C(9)	0.911(4)	0.567(2)	0.792(4)	5.7(7)		
C(10)	1.008(4)	0.526(2)	0.712(3)	6.5(8)		
C(11)	1.28(3)	0.309(2)	0.880(3)	4.0(5)		
C(12)	1.287(4)	0.270(2)	1.008(3)	4.9(6)		
C(13)	1.372(4)	0.200(2)	0.939(4)	6.6(8)		
C(14)	1.317(5)	0.174(2)	0.782(5)	7.1(9)		
C(15)	1.167(5)	0.209(3)	0.662(5)	7.6(10)		
C(16)	1.074(3)	0.273(2)	0.708(3)	4.5(6)		
C(17)	0.901(3)	0.318(2)	0.568(3)	4.7(6)		
C(18)	0.692(3)	0.256(2)	0.682(4)	4.7(6)		
C(19)	0.622(4)	0.408(3)	0.513(4)	6.7(7)		
N	0.770(2)	0.342(1)	0.647(2)	3.6(4)		
	U_{11}^a	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti	3.6(2)	2.1(1)	2.5(1)	-1.6(2)	1.6(1)	-0.4(2)

$$^a T(hkl) = \exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2ha^*kb^*U_{12} + \dots)].$$

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