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STRUCTURE OF μ-DINITROGENBIS[p-TOLYLDICYCLOPENTADIENYLTITANIUM(III)], $[(C_5H_5)_2Ti(p\text{-}CH_3C_6H_4)]_2N_2$

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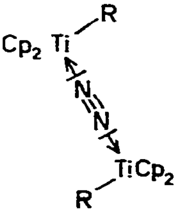
Summary

An X-ray diffraction study of μ-dinitrogenbis[p-tolyldicyclopentadienyltitanium(III)], $[(C_5H_5)_2Ti(p\text{-}CH_3C_6H_4)]_2N_2$, shows that the two titanium atoms in the molecule are linked by the dinitrogen ligand in an essentially linear manner. The titanium atoms have a pseudo-tetrahedral environment. The cyclopentadienyl rings are π-bonded to the Ti atoms; the ring planes are mutually inclined at an angle of 42.8°. The aryl groups are σ-bonded to the Ti atoms and are coplanar with the TiN≡NTi unit within 0.12 Å. Important bond lengths are Ti—N 1.962(6), N—N 1.162(12), Ti—C(σ) 2.216(7), Ti—10 C(C_5H_5) 2.355—2.380 Å.

Introduction

The synthesis and properties of the dinitrogen complexes $[(C_5H_5)_2TiR]_2N_2$, where R is an aryl group, were described previously [1]. The diamagnetic complexes proved to be capable of activating the coordinated dinitrogen with respect to reduction to hydrazine or ammonia; the mechanism of this reduction has been investigated in detail [2]. However, the structure of the complexes $[(C_5H_5)_2TiR]_2N_2$, particularly the bonding of the dinitrogen group, remained uncertain. The absence of a N≡N stretching vibration in the IR spectrum sug-



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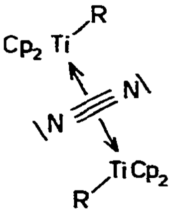

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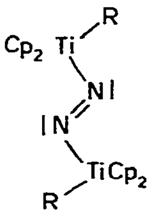

(3)

gests a centrosymmetric coordination of the dinitrogen molecule, which can be achieved in a *monohapto* (end-on) (1) or in a *dihapto* (edge-on) fashion (2) with trivalent titanium in both cases. Also possible is an arrangement with the N_2 ligand in an intermediate position (3), with Ti—N single bonds giving formally tetravalent titanium.

In order to establish the exact Ti—N_2—Ti arrangement an X-ray crystal structure determination of the title compound was undertaken.

The molecular structure

The molecular structure of $[(C_5H_5)_2Ti(p\text{-}CH_3C_6H_4)]_2N_2$ and atom numbering scheme are shown in Fig. 1. The bond lengths and angles are listed in Table 1. The binuclear molecule consists of two $(C_5H_5)_2Ti(p\text{-}CH_3C_6H_4)$ entities bridged by the dinitrogen ligand in an essentially linear manner. The two halves of the molecule are related by a (crystallographic) centre of symmetry. From Fig. 1 and Table 1 it can be inferred that both five-membered rings are π-bonded to the metal. The average distances from Ti to the carbon atoms of the rings II and III (definitions of the rings are given in Table 2a) are 2.374(7) and 2.370(8) Å,

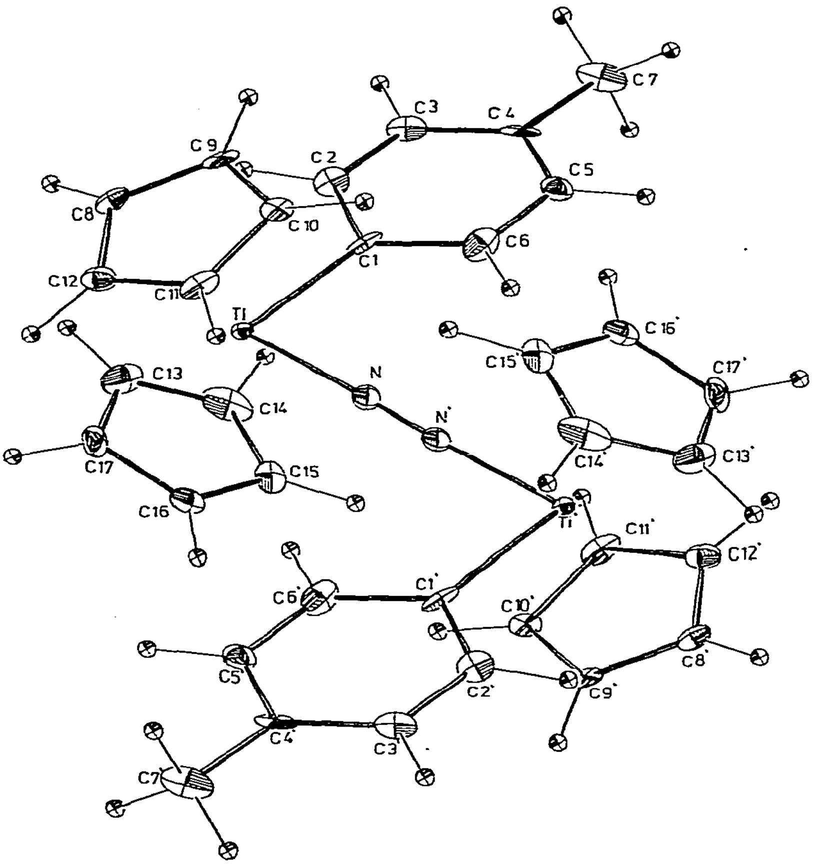

Fig. 1. Structure of the molecule.

TABLE 1

BOND DISTANCES AND BOND ANGLES

Bond distances [a] (Å)		Bond angles [a] (deg)	
Ti—N	1.962(6)	Ti—N—N′	176.5(5)
N—N′	1.162(12)	N—Ti—RC(II)	104.0
Ti—RC(II) [b]	2.048	N—Ti—RC(III)	104.5
Ti—RC(III) [b]	2.049	N—Ti—C(1)	91.1(2)
Ti—C(1)	2.216(7)	C(1)—Ti—RC(II)	103.5
Ti—C(8)	2.379(7)	C(1)—Ti—RC(III)	106.2
Ti—C(9)	2.371(7)	RC(II)—Ti—RC(III)	137.9
Ti—C(10)	2.375(7)	Ti—C(1)—C(2)	123.2(5)
Ti—C(11)	2.380(7)	Ti—C(1)—C(6)	122.2(5)
Ti—C(12)	2.363(7)	C(2)—C(1)—C(6)	114.6(6)
Ti—C(13)	2.355(9)	C(1)—C(2)—C(3)	122.5(7)
Ti—C(14)	2.379(8)	C(2)—C(3)—C(4)	120.9(7)
Ti—C(15)	2.374(8)	C(3)—C(4)—C(5)	118.4(6)
Ti—C(16)	2.370(7)	C(3)—C(4)—C(7)	120.8(7)
Ti—C(17)	2.362(8)	C(5)—C(4)—C(7)	120.7(7)
C(1)—C(2)	1.408(9)	C(4)—C(5)—C(6)	120.2(7)
C(2)—C(3)	1.391(10)	C(1)—C(6)—C(5)	123.4(6)
C(3)—C(4)	1.397(11)	C(8)—C(9)—C(10)	109.4(6)
C(4)—C(5)	1.387(10)	C(9)—C(10)—C(11)	107.4(6)
C(5)—C(6)	1.388(10)	C(10)—C(11)—C(12)	107.2(6)
C(6)—C(1)	1.417(10)	C(11)—C(12)—C(8)	109.0(6)
C(4)—C(7)	1.519(10)	C(12)—C(8)—C(9)	107.1(6)
C(8)—C(9)	1.397(10)	C(13)—C(14)—C(15)	108.7(7)
C(9)—C(10)	1.409(10)	C(14)—C(15)—C(16)	107.2(6)
C(10)—C(11)	1.427(10)	C(15)—C(16)—C(17)	108.4(7)
C(11)—C(12)	1.405(10)	C(16)—C(17)—C(13)	107.8(6)
C(12)—C(8)	1.418(10)	C(17)—C(13)—C(14)	107.8(7)
C(13)—C(14)	1.380(11)		
C(14)—C(15)	1.401(11)		
C(15)—C(16)	1.402(10)		
C(16)—C(17)	1.385(10)		
C(17)—C(13)	1.411(11)		

[a] Standard deviations in parentheses are in units of the last decimal place. [b] RC(II) = C(8)—C(12) ring centroid; RC(III) = C(13)—C(17) ring centroid.

respectively, which are normal values for this type of compound. The rings are planar and quite regular; the bond angles are close to 108° and the bonded C—C distances within the rings are in the range 1.397—1.427 Å (average value 1.411(10) Å) for ring II and in the range 1.380—1.411 Å (average value 1.396(11) Å) for ring III. Table 2b gives the distance of the atoms from the least-squares planes of the rings. The Ti atom lies at 2.048 and 2.049 Å from the two rings, and these distances are also the Ti rings centroid distances (Table 1). The values are in accord with the average value of 2.045 Å derived from eight other $(C_5H_5)_2TiR_{(n)}$ complexes with Ti d^1 configurations [3]. The two Ti ring centroid vectors include an angle of 137.9°, while the dihedral angle between the ring planes is 42.8° (Table 2c).

The phenyl ring is σ-bonded to the metal atom. The Ti—C(1) σ-bond length of 2.216(7) Å is consistent with the values found in other aryldicyclopentadienyltitanium compounds; for instance the distances in $(C_5H_5)_2Ti\{2,6\text{-}(CH_3)_2\text{-}C_6H_4\}$ [4] and $(C_5H_5)_2Ti[2\text{-}\{(CH_3)_2NCH_2\}\text{-}C_6H_4]$ [5] are 2.178(7) and 2.22(3) Å, respectively. The phenyl group is planar, but the carbon atom of the methyl

TABLE 2

LEAST SQUARES PLANES [a], [b]

(a) Equations of the planes

Atoms	Plane	P	Q	R	S
C(1) ... C(6)	I	0.6319	0.7145	−0.3003	0.2468
C(8) ... C(12)	II	0.6513	0.7577	−0.0415	2.6465
C(13) ... C(17)	III	0.6007	0.4150	−0.6834	−2.6988
Ti, N, C(1) ... C(7), Ti′, N′, C(1)′ ... C(7)′	IV	0.6765	0.6594	−0.3280	0.0
Ti, RC(II), RC(III)	V	−0.7381	0.6170	−0.2732	1.8748
Ti, C(1), N	VI	0.6825	0.6337	−0.3642	−0.0077

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

Atoms plane I		Atoms plane II		Atoms plane III		Atoms plane IV	
C(1)	−0.004	C(8)	0.003	C(13)	0.008	Ti	0.09
C(2)	0.006	C(9)	0.0	C(14)	−0.009	N	0.01
C(3)	−0.004	C(10)	−0.003	C(15)	0.007	C(1)	0.03
C(4)	−0.001	C(11)	0.004	C(16)	−0.002	C(2)	−0.05
C(5)	0.003	C(12)	−0.004	C(17)	−0.003	C(3)	−0.07
C(6)	−0.001	Ti	−2.048	Ti	2.049	C(4)	0.02
C(7)	−0.099	H(8)	−0.07	H(13)	−0.01	C(5)	0.12
N	−0.190	H(9)	0.03	H(14)	0.15	C(6)	0.12
Ti	0.032	H(10)	−0.09	H(15)	0.13	C(7)	−0.09
H(2)	0.18	H(11)	0.0	H(16)	−0.02		
H(3)	−0.01	H(12)	−0.21	H(17)	−0.27		
H(5)	−0.10						
H(6)	0.05						
H(71)	0.47						
H(72)	0.30						
H(73)	−1.14						

(c) Dihedral angles (deg)

I ... II 15.1; I ... III 28.2; I ... IV 4.4; I ... V 86.8; I ... VI 6.6; II ... III 42.8;
II ... IV 17.5; II ... VI 20.0; III ... IV 25.3; III ... VI 22.8; IV ... V 89.8; IV ... VI 2.6;
V ... VI 89.2

[a] The equations of the planes are $PI + QJ + RK = S$ in orthogonal Ångström space where P, Q, and R are direction cosines, referred to orthogonal axes system I, J and K, where I, J and K are unity vectors, with I // a, J // b and K // c*. [b] Hydrogen atoms bear the same number as the carbon atoms to which they are attached; H(71), (72) and (73) are attached to C(7).

group does not quite lie in the ring plane (see Table 2b). The C—CH$_3$ distance is normal, and the C—C bond lengths lie in a narrow range and average 1.397(10) Å. Except for the small value of the endocyclic angle C(2)—C(1)—C(6), 114.6°, which has been rationalized previously on the basis of the electropositivity of the metal atom [6], there is no distortion around atom C(1), as has been observed in related complexes [4,7].

Figure 2 shows the geometry of the ligands about the metal atoms. If the two C$_5$H$_5$ rings are considered to occupy one coordination site each, the coordination about the Ti atoms is that of a severely distorted tetrahedron, as usually found in (C$_5$H$_5$)$_2$ML$_2$ complexes. The distortion is seen from the values of the

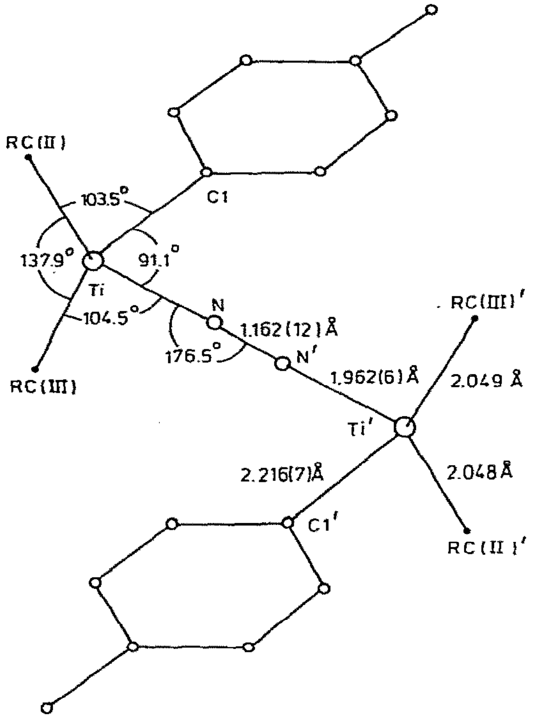

Fig. 2. Skeletal view of $[(C_5H_5)_2Ti(p\text{-}CH_3C_6H_4)]_2N_2$.

angles RC(II)—Ti—RC(III) 137.9°, and N—Ti—C(1) 91.1°. The plane containing the Ti atom and the ring centroids (V) is perpendicular to that containing the Ti—N and Ti—C vectors (VI) and bisects the N—Ti—C(1) angle, while the N—Ti—C(1) plane nearly bisects the angle between the two cyclopentadienyl rings (Table 2).

Of great interest in this structure is the presence of a plane (IV) defined by the Ti, N and C (tolyl group) atoms of both halves of the dimer (planar to 0.12 Å). This remarkable feature causes back bonding of both Ti atoms to the same π^* orbital of the N_2 ligand (and causes therefore the diamagnetism of the complex), and probably also makes possible delocalization of π electrons from the N_2 ligand via the Ti atoms to the phenyl groups (see the bonding scheme discussed later). Therefore the Ti-phenyl system may be involved in the charge transfer band ($\epsilon > 10^4$ l mol cm^{-1}) at about 600 nm which is responsible for the intense blue colour of the complex studied and related titanium-dinitrogen complexes [1,8,9]. Work is in progress to investigate the resonance Raman spectra of the compounds $[(C_5H_5)_2TiR]_2N_2$ (where R is an aryl group) to settle this issue.

The Ti—N bond length of 1.962(6) Å clearly shows the presence of a Ti—N σ bond; it agrees closely with the average Ti—N distance of 2.017(12) Å in the only other structurally characterized titanium dinitrogen complex $[\{(CH_3)_5C_5\}\text{-}Ti]_2N_2$ [10]. These bond lengths can be compared to those in the diazido [11], isocyanato [12] and thiocyanato [13] complexes of the $(C_5H_5)_2Ti^{IV}$ group (Table 3). A considerably longer Ti—N distance is found in the amino complexes $(C_5H_5)_2Ti[2\text{-}\{(CH_3)_2NCH_2\}C_6H_4]$ [5] and $(C_5H_5)Ti[2\text{-}\{(CH_3)_2NCH_2\}C_6H_4]_2$

TABLE 3

SUMMARY OF Ti—N AND N—N BOND LENGTHS (Å) IN (DI)NITROGEN COMPLEXES OF TITANIUM

	Ti—N	N—N	Ref.
$[(C_5H_5)_2Ti^{III}(p\text{-}CH_3C_9H_4)]_2N_2$	1.962(6)	1.162(12)	
$[\{(CH_3)_5C_5\}_2Ti^{II}]_2N_2$ [a]	2.017(12) [b]	1.160(14)	10
$(C_5H_5)_2Ti^{IV}(N_3)_2$	2.03(1)	1.18(2) 1.10(2)	11
$(C_5H_5)_2Ti^{IV}(NCO)_2$	2.012(3) [b]		12
$(C_5H_5)_2Ti^{IV}(NCS)_2$	2.021(7)		13
$(C_5H_5)_2Ti^{III}[2\text{-}\{(CH_3)_2NCH_2\}C_6H_4]$	2.46(2)		5
$(C_5H_5)Ti^{III}[2\text{-}\{(CH_3)_2NCH_2\}C_6H_4]_2$	2.389(4)		14
$[\{(C_2H_5)_2N\}_3Ti^{IV}C_5H_4]_2Fe$	1.89 [b]		15
$Ti^{IV}Cl_3\{N(C_2H_5)_2\}$	1.852		16
$N\equiv N(N_2)$		1.0976	29
$N=N(CH_3N=N\text{-}CH_3)$		1.23	30
$N—N(N_2H_4)$		1.46	30

[a] Two molecules in the asymmetric unit. [b] Average value.

[14], 2.46 Å and 2.39 Å, respectively, whereas for the amido complexes $[\{(C_2H_5)_2N\}_3TiC_5H_4]_2Fe$ and $TiCl_3\{N(C_2H_5)_2\}$ significantly shorter Ti—N distances have been reported, 1.89 Å (average value) and 1.85 Å [15,16], respectively. The $N(C_2H_5)_2$ groups are planar, allowing some double bond character to be involved in the Ti—N bonds. The N—N bond length of 1.162(12) Å in our compound corresponds with the values of 1.160(7) Å and 1.182(5) Å found for the bridging dinitrogen ligands in $[(Me_5C_5)_2Ti]_2N_2$ [10] and $[(Me_5C_5)_2ZrN_2]_2N_2$ [17]. A comparison with the N—N bond lengths in other binuclear complexes shows similar values for the N—N distances in $(Me_3P)_3CoN_2K$, 1.16—1.18 Å [18] and $(PhMe_2P)_4ReCl(N_2)MoCl_4(OMe)$, 1.18 Å [19], while somewhat shorter N—N distances of 1.12 Å have been observed in $[(C_5H_5)Mn(CO)_2]_2N_2$ [20], $[\{(C_6H_{11})_3P\}_2Ni]_2N_2$ [21] and $[\{(NH_3)_5Ru\}_2N_2](BF_4)_4$ [22].

Relation to nitrogen reduction

The significant lengthening of the N—N bond upon coordination compared to that in the free molecule (1.0976 Å) suggests a weakening of the N—N triple bond, although the distance corresponding to a N—N double bond (1.23 Å) is not reached. In the compounds $[(C_5H_5)_2TiR]_2N_2$ the reduction of the N—N bond order does not seem to play a deciding role in the activation of the fixed N_2 molecule towards reduction. Van der Weij concluded from a study of the reduction by bulky reducing agents such as NaC_8H_{10} and n-BuLi, that the first step in the reduction is the removal of one of the C_5H_5 groups per titanium, while the N—N bond and Ti—phenyl σ bond are retained [2]. Fig. 1 shows the structure of $[(C_5H_5)_2Ti(p\text{-}CH_3C_6H_4)]_2N_2$ to be rather compact and, therefore, it seems plausible that, in addition to a low tendency for the TiN_2Ti system to accommodate additional electrons, steric factors inhibit the attack on the N_2

ligand in the first stage of the reduction. Also, the facile displacement of the strongly activated dinitrogen (N—N 1.35 Å) by ethylene observed in $\{[(C_6H_5Li)_3Ni]_2N_2 \cdot 2[O(C_2H_5)_2]\}_2$ [23], indicates a reduction of the N—N bond order to be of minor importance in nitrogen fixation. In mononuclear dinitrogen complexes on the other hand, even a small decrease in the N—N bond order may result in an activation of the ligated dinitrogen sufficient for it to undergo further reactions. For instance, in some dinitrogen complexes of molybdenum and tungsten, in which N_2 is substantially polarized by coordination, protonation of the terminal nitrogen is achieved in reactions with hydrogen halides [24]. Protonation of dinitrogen to hydrazine in $[(Me_5C_5)_2ZrN_2]_2N_2$ [25] with both terminal and bridging N_2 ligands coordinated to the same metal, also points to a decisive part of the slightly altered terminal dinitrogen groups. Attempts to protonate the dinitrogen ligand in $[(C_5H_5)_2TiR]_2N_2$ with acids like HCl led to the liberation of the complexed nitrogen [1,26], probably because of an attack by the proton on another part of the molecule, e.g. atom C(1) of the aryl group.

Bonding scheme

Figure 3 presents a bonding picture of $[(C_5H_5)_2Ti(p\text{-}CH_3C_6H_4)]_2N_2$. The fact that the Ti, C(1) and N atoms are in the plane bisecting the angle between the cyclopentadienyl rings allows the application of the bonding model of bent $(C_5H_5)_2M$ complexes, as formulated by Lauher and Hoffmann [27]. The three low-energy frontier orbitals for an eclipsed-ring geometry of the $(C_5H_5)_2M$ group (C_{2v} symmetry) have a significant extent in the yz plane (Fig. 3a). Each of the two titanium atoms will form two σ bonds with the N_2 and phenyl ligands of the two metals using the $2a_1$ and b_2 orbitals (Fig. 3b). The $1a_1$ orbitals which contain one electron each, are now of proper symmetry to be stabilized by combination with the in-plane π^* orbital of N_2 (Fig. 3c). This "back-bonding" reduces the strength of the N—N bond, but the N—N bond order remains larger than two (for a N—N bond order of two Ti would become formally tetravalent). Since both Ti atoms interact with the in-plane π^* orbital of N_2 in the way described, it is understandable that the spins of their odd electrons (in the $1a_1$ orbitals) are strongly coupled, making $[(C_5H_5)_2Ti(p\text{-}CH_3C_6H_4)]_2N_2$ a diamagnet. The bonding scheme presented resembles that already developed for transition metal dinitrogen complexes. Population of empty metal orbitals by a σ donation of the N_2 lone pair results in an increased electron density on the metal, which is in turn reduced by back-donation from partly filled metal d orbitals into the antibonding π orbitals of N_2 (synergic).

Bercaw et al. [10,17] have proposed an interaction of the empty b_1 and a_2 orbitals with filled N_2 π orbitals in $[(Me_5C_5)_2Ti]_2N_2$ and $[(Me_5C_5)_2ZrN_2]_2N_2$, which allows an additional delocalization of the charge build-up from one metal atom via N_2 orbitals into empty π orbitals of the other metal atom ("push—pull" interaction). Such a charge transfer across the TiN≡NTi unit is not possible in our centrosymmetric compound, which reveals no torsion angles along the Ti—Ti line, but there may exist a N_2—Ti—C(1) π interaction of a similar type (Fig. 3d, e) which links the π systems of the aryl and dinitrogen ligands perpendicular to the (Ti, N, C(1)) plane. As mentioned above, this will be the subject of a further study.

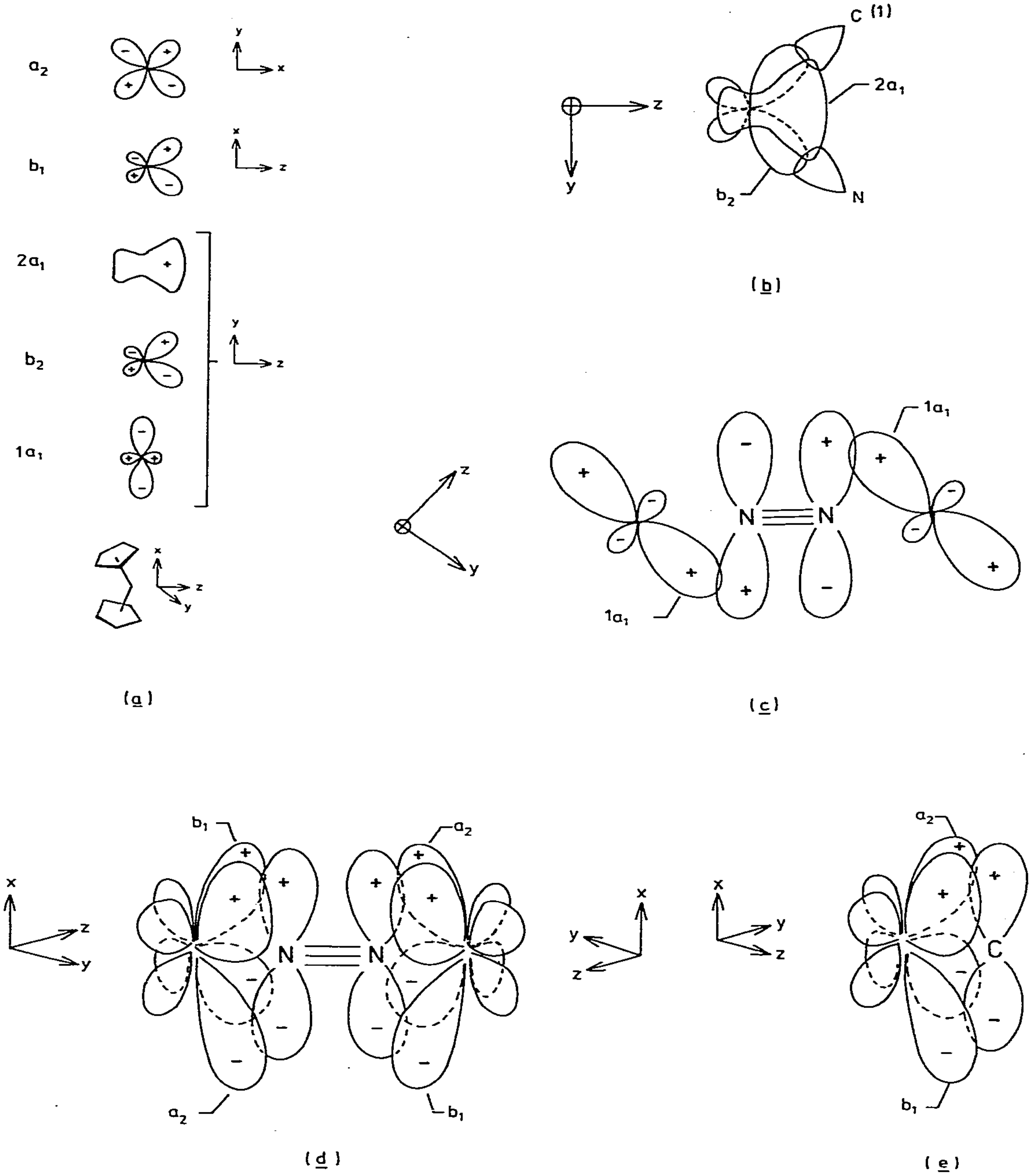

Fig. 3. (a) Contours of the five frontier orbitals of a bent eclipsed $(C_5H_5)_2Ti$ fragment (C_{2v} symmetry); the (x, z) plane is defined by the two metal ring centroid vectors, the z axis bisecting the angle between these two vectors. (b) Formation of the Ti—N (sp) and Ti—C (sp^2) σ bonds using the $2a_1$ and b_2 titanium orbitals. (c, d) Interactions of the N_2 p_π orbitals with the $1a_1$, a_2, and b_1 titanium orbitals. The a_2 and b_1 orbitals lie in the (x, y) and (x, z) planes, respectively. (e) Interaction of the C(1) p_π orbital with the a_2 and b_1 titanium orbitals.

Experimental

The complexes $[(C_5H_5)_2TiR]_2N_2$ with R = C_6H_5, *m*-, *p*-$CH_3C_6H_4$ were prepared from $(C_5H_5)_2TiCl_2$ by a modification of the original method [1]. The X-ray analysis was hampered by difficulties in obtaining single crystals. Numerous attempts were made using various solvents. Only in the case of R = *p*-tolyl did we succeed in obtaining satisfactory crystals. Further attempts to prepare crystals of the related compounds $[(CH_3C_5H_4)_2TiR]_2N_2$ were also unsuccessful. $[(C_5H_5)_2Ti(p\text{-}CH_3C_6H_4)]_2N_2$ was isolated as ill-formed crystals with a metallic lustre, by slowly cooling a pentane solution of the nitrogen-free complex $(C_5H_5)_2$-$Ti(p\text{-}CH_3C_6H_4)$ (0° C) in a N_2 atmosphere. Because of the extreme sensitivity of the compound towards oxygen and water, the crystals were mounted in thin-walled glass capillaries. The handling of the crystals was seriously hampered by their fragility and irregular dimensions. Crystallographic data are given in Table 4. No reliable value of the density could be determined due to the decomposition of the compound during the measurements; the calculated value of 1.36 g/cm^3 is, however, a reasonable value for compounds of this type.

The position of the Ti atom was deduced from an unsharpened three-dimensional Patterson map. After anisotropic refinement of the Ti parameters, the positions of the nitrogen atom and of some carbon atoms could be read from a Fourier synthesis of reflections with reliable sign. The remaining C atoms were found from two successive difference Fourier maps calculated after anisotropic refinement of Ti, N and C obtained from the previous maps. Up to this point full least-squares anisotropic refinement of all non-hydrogen parameters still developed non-positive temperature factors for three carbon atoms. Examination of the correlation matrix showed no correlation coefficients of significant magnitude between the carbon coordinates. A check of the $F_0 - F_c$ list revealed a number of reflections with remarkably high values of F_0, presumably due to some failure during the measurements of the intensities.

Because a new collection of intensity data was not feasible, we decided to discard henceforth 86 reflections with $F_0 - F_c > 3\sigma(F)$. This procedure may

TABLE 4

CRYSTALLOGRAPHIC DATA AND DETAILS OF EXPERIMENTAL METHODS

Data	Experimental details
Monoclinic Spacegroup $P2_1/C$	Weissenberg photographs
T = 90 K a = 8.093(3) Å b = 17.799(10) Å c = 9.678(5) Å β = 96.40(4)°	Least-squares refinement of $\sin^2\theta$ values from 25 reflections from counter data with $\lambda(\text{Mo-}K_{\alpha_1})$ 0.70926 Å and $\lambda(\text{Mo-}K_{\alpha_2})$ 0.71354 Å
$Z = 2[(C_5H_5)_2Ti(p\text{-}CH_3C_6H_4]_2N_2$ D_x = 1.358 g/cm^3	
4248 intensities	Automatic Nonius CAD-4 diffractometer, Zr-filtered Mo-radiation, ω-scan, $\sin\theta/\lambda < 0.7034$ Å^{-1}. Reflections with I(net) $\leqslant 0$ were hereafter discarded.
2081 independent $F(hkl)$ values $\lvert F \rvert > 3\sigma(\lvert F \rvert)$	Corrections for L.P. factors; no absorption correction (μ(Mo) = 6.5 cm^{-1}). Dimensions crystal: 0.005—0.02 cm.

TABLE 5. FINAL PARAMETERS: COORDINATES, TEMPERATURE PARAMETERS B OF THE HYDROGEN ATOMS, AND PARAMETERS U_{ij} OF THE TEMPERATURE FACTOR OF THE NON-HYDROGEN ATOMS. Parameters U_{ij} (10^{-3} Å^2) are coefficients of the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots ha^*kb^*U_{12} \ldots)]$

Atom	x/a	y/b	z/c	B (Å^2)	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{13}$	$2U_{23}$
Tl	−0.14466(16)[a]	0.10950(7)	0.10468(13)		6.3(6)	5.5(5)	7.3(6)	0(1)	0(1)	1(1)
N	−0.0356(8)	0.0249(3)	0.0218(6)		18(4)	11(3)	11(3)	−8(5)	8(6)	2(5)
C(1)	−0.3198(8)	0.1234(3)	−0.0866(7)		11(4)	3(4)	27(5)	0(5)	12(7)	−2(6)
C(2)	−0.4529(8)	0.1747(4)	−0.0974(8)		9(4)	15(4)	21(4)	−1(6)	3(6)	0(7)
C(3)	−0.5609(9)	0.1833(4)	−0.2187(8)		7(4)	15(4)	22(4)	−4(6)	2(6)	12(7)
C(4)	−0.5397(9)	0.1416(4)	−0.3377(8)		19(4)	11(4)	18(4)	−11(6)	6(7)	23(6)
C(5)	−0.4088(9)	0.0909(4)	−0.3318(7)		18(4)	14(4)	13(4)	−8(6)	3(6)	7(6)
C(6)	−0.3029(9)	0.0823(4)	−0.2097(8)		14(4)	16(4)	27(5)	0(6)	17(7)	−7(7)
C(7)	−0.6638(9)	0.1475(5)	−0.4671(8)		12(4)	31(5)	27(5)	−3(8)	0(7)	26(8)
C(8)	−0.0737(8)	0.2375(4)	0.1502(7)		7(4)	7(3)	22(4)	−5(6)	−3(6)	−3(6)
C(9)	−0.0743(10)	0.2259(4)	0.0074(8)		22(4)	4(3)	23(4)	−13(6)	17(7)	5(6)
C(10)	0.0520(8)	0.1744(4)	−0.0158(7)		11(4)	10(3)	16(4)	−13(6)	16(6)	6(6)
C(11)	0.1342(8)	0.1537(4)	0.1169(8)		3(3)	9(4)	29(4)	−8(6)	12(6)	−2(7)
C(12)	0.0549(8)	0.1922(4)	0.2178(8)		12(4)	12(4)	18(4)	−6(6)	−3(6)	6(6)
C(13)	−0.3375(10)	0.1205(4)	0.2688(8)		44(5)	15(5)	29(5)	13(8)	53(8)	5(7)
C(14)	−0.4025(9)	0.0677(5)	0.1733(8)		12(4)	36(5)	26(5)	4(7)	27(7)	29(8)
C(15)	−0.2956(9)	0.0056(4)	0.1796(8)		23(4)	20(4)	14(4)	−28(7)	21(7)	−4(7)
C(16)	−0.1650(9)	0.0203(4)	0.2838(7)		25(5)	17(4)	14(4)	−4(7)	5(7)	10(6)
C(17)	−0.1900(10)	0.0907(4)	0.3391(7)		37(5)	18(4)	11(4)	−20(7)	24(7)	−7(7)
H(2)	−0.4576	0.2137	−0.0125	2(2)						
H(3)	−0.6633	0.2224	−0.2238	1(1)						
H(5)	−0.4007	0.0550	−0.4206	5(2)						
H(6)	−0.1980	0.0447	−0.2083	0(1)						
H(71)	−0.6004	0.1409	−0.5588	4(2)						
H(72)	−0.7236	0.2018	−0.4704	5(2)						
H(73)	−0.7555	0.1037	−0.4635	2(2)						
H(8)	−0.1596	0.2702	0.2035	1(1)						
H(9)	−0.1606	0.2561	−0.0656	4(2)						
H(10)	0.0801	0.1491	−0.1118	4(2)						
H(11)	0.2370	0.1150	0.1354	5(2)						
H(12)	0.0702	0.1800	0.3278	2(2)						
H(13)	−0.3909	0.1744	0.2898	1(1)						
H(14)	−0.5054	0.0847	0.0991	4(2)						
H(15)	−0.3060	−0.0409	0.1075	1(1)						
H(16)	−0.0659	−0.0193	0.3120	2(2)						
H(17)	−0.1273	0.1098	0.4372	3(2)						

not be a desirable one, because more observations may suffer from the experimental errors, leading to somewhat strange temperature factors. However, the positional atomic parameters derived with or without the 86 reflections mentioned do not differ significantly, which justifies the procedure followed. A subsequent difference map of low-angle reflections only showed the positions of six ring hydrogen atoms and one hydrogen of the methyl group. The positions of the two unresolved methyl hydrogen atoms were calculated, assuming a tetrahedral geometry about C(7). The positions of the remaining H atoms could be detected from two new difference maps. The H atoms were then placed at a distance of 1.08 Å from the corresponding C atom, without changing the observed C—H directions; they were included in the subsequent refinement cycles with fixed positions, only their *B* values were refined. During the final refinement cycles, the weighing scheme $W = [W_c^{-1} + 0.0005\ |F|^2]^{-1}$ was applied, W_c being the weight of the individual reflections based on counting statistics. The index $R = [\Sigma(\Delta F)^2/\Sigma F_0^2]^{1/2}$ decreased to 0.107 and the weighed index $R_w = [\Sigma W(\Delta F)^2/\Sigma WF_0^2]^{1/2}$ to 0.077, based on 1995 reflections. The final coordinates and temperature factors and their standard deviations are listed in Table 5. A list of observed and calculated structure factors is available from the authors on request. All calculations were performed on a Cyber 74-16 with the X-ray 1975 [28] system.

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