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Crystal structures of titanocene 2,2′-bipyridyl complexes. Singlet versus triplet state-dependence on methyl substituents at the cyclopentadienyl ligands [1]

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Abstract

The X-ray diffraction analysis of titanocene-2,2′-bipyridyl complexes $(C_5H_5)_2Ti(bpy)$ (**1**), $(C_5HMe_4)_2Ti(bpy)$ (**2**) and $(C_5Me_5)_2Ti(bpy)$ (**3**) revealed that the bpy ligand is inclined to one of the cyclopentadienyl ligands in **1** and **2** whereas in **3** it lies in the plane bisecting the CE–Ti–CE angle of the titanocene skeleton. The triplet state ESR signal of solid **3** grows in intensity while those of **1** and **2** decrease in intensity with lowering of temperature down to 77 K. This behaviour shows that the symmetrical position of bpy ligand in **3** is associated with a ground triplet state and the asymmetrical position in **1** and **2** with a ground singlet state. The relation of the spin state of titanocene–bpy complexes to their structure as deduced by McPherson et al. [A.M. McPherson, B.F. Fieselmann, D.L. Lichtenberger, G.L. McPherson and G.D. Stucky, J. Am. Chem. Soc., 101 (1979) 3425] from properties of **1** has thus been confirmed. © 1998 Elsevier Science S.A.

Keywords: Cyclopentadienyl ligands; Titanocene; Bpy ligands

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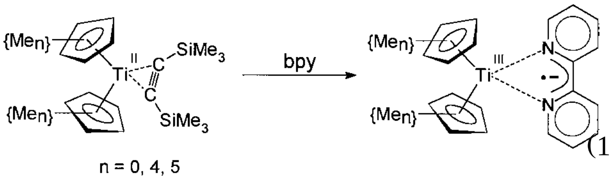
1. Introduction

Titanocene (Ti^{II}) complexes suffer from a low stability resulting from the presence of easily available d^2 electrons. Only those compounds which contain ligands capable to accommodate these electrons in their π^*-orbitals (back bonding) [1] show a good thermal stability at moderate temperatures. Well-known examples are titanocene dicarbonyls [2], titanocene bis(trimethylphosphane) [3], and titanocene acetylene complexes as well as the complexes with combined ligands of these types [4]. A thermally stable titanocene complex with 2,2′-bipyridyl (bpy) $(C_5H_5)_2Ti(bpy)$ (**1**) does not belong to this class of compounds although it arises from the reactions of $(C_5H_5)_2TiCl_2$ with dilithium salt of bpy dianion [5], $(C_5H_5)_2Ti(CO)_2$ with bpy [6] or $(C_5H_5)_2Ti(Me_3SiC{\equiv}CSiMe_3)$ with bpy [7], all of which should lead to a Ti(II) product. A fundamental study by McPherson et al. [8] revealed that complex **1** exerts the ESR spectrum of an electronic triplet state in frozen toluene glass at 123–104 K and that a further lowering of the temperature to 77 K leads to a sharp decrease in the spectrum intensity. These results led to the conclusion that one of two *d*-electrons is transferred to the bpy ligand to give a radical anion. The latter remains coupled with the d^1 electron at the Ti(III) centre to give a system of two remote electrons in interaction.



(1)

The system forms a ground singlet state $(S = 0)$ at 77 K, and at higher temperatures a triplet state $(S = 1)$ showing a typical ESR spectrum. The zero field split-

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[1] Dedicated to Professor P.M. Maitlis on the occasion of his 65th birthday.

ting $D = 0.0412$ cm^{-1} obtained for **1** in toluene glass implies the distance between the two electrons close to 3.5 Å, provided the electron interaction is dipolar only. This distance is much longer than the Ti–N distance of 2.14 Å determined by a preliminary X-ray diffraction analysis; however, the delocalisation of one electron over two nitrogen atoms of bpy can account for the difference. The X-ray analysis also established that the molecular plane of the bpy ligand is declined from the plane bisecting the CE–Ti–CE (CE-centroid of the C_5H_5 ring) angle by ca. 25°. Since the intensity of the triplet state ESR spectrum was low and was further decreasing with lowering of temperature, the bent structure has been attributed to a ground singlet state. This conclusion was also supported by quantum chemical calculations suggesting the bent structure for the singlet state and the symmetrical (C_{2v}) structure for the triplet state [8]. Unfortunately, the diffraction data for **1** are not of standard accuracy and the study lacks any evidence for the molecular structure in triplet state.

We have recently reported that $(C_5HMe_4)_2Ti(bpy)$ (**2**) and $(C_5Me_5)_2Ti(bpy)$ (**3**) show more intense triplet state ESR spectra in toluene glass than **1**, and that with lowering of the temperature the spectrum intensity of **2** decreases and that of **3** increases [7]. This offered us the opportunity to examine justification of the above suggestion [8] associating the ground spin state to the position of the bpy ligand in titanocene–bpy complexes.

Here, we report the X-ray crystal structures of compounds **1**, **2** and **3** and temperature dependences of the ESR spectra of these compounds in the solid state with the aim to correlate the position of bpy ligand with the electronic spin state.

2. Experimental

2.1. General data and methods

The synthesis, purification and crystallisation procedures and the measurements of EPR and UV–NIR spectra in solutions were carried out in evacuated all-sealed glass devices equipped with magnetically breakable seals. A combined device equipped with a pair of quartz cuvettes (1 cm and 1 mm) and a quartz ESR tube was used for UV–NIR and ESR measurements. ESR spectra were recorded on an ERS-220 spectrometer (Centre for Production of Scientific Instruments, Academy of Sciences of GDR, Berlin, Germany) operated by a CU-1 unit (Magnettech, Berlin, Germany) in the X-band. g-Values were determined using an Mn^{2+}

Table 1
Crystal and structure refinement data for **1–3**

	1	**2**	**3**
Crystal data			
Chemical formula	$C_{20}H_{18}N_2Ti$	$C_{28}H_{34}N_2Ti$	$C_{30}H_{38}N_2Ti$
Mol. wt. (gmol^{-1})	334.27	446.47	474.52
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	*Iba*2, No. 45	*Pnma*, No. 62	*Pbca*, No. 61
a (Å)	16.6462(12)	17.6671(9)	16.667(2)
b (Å)	27.691(2)	17.232(2)	29.891(3)
c (Å)]	7.7914(9)	15.309(2)	20.873(5)
V (Å^3)	3591.5(6)	4660.6(8)	10399(3)
Z	8	8	16
$D_{calc.}$ (g cm^{-3})	1.236	1.273	1.212
μ(Mo–K$_\alpha$)(mm^{-1})	0.477	0.385	0.349
F(000) (e)	1392	1904	4064
Crystal colour and habit	brown, platelet	brown, platelet	brown, platelet
Approximate crystal size (mm^3)	$0.8 \times 0.4 \times 0.2$	$0.6 \times 0.5 \times 0.4$	$0.5 \times 0.5 \times 0.3$
Temperature (K)	295	295	295
Data collection and refinement			
θ-range for data collection (deg)	1.43 to 24.97	1.76 to 24.97	1.36 to 24.97
h, k, l range	$0 \to 19$, $-32 \to 32$, $0 \to 9$	$0 \to 20$, $0 \to 20$, $-18 \to 0$	$0 \to 19$, $-35 \to 0$, $0 \to 24$
Reflections collected	3358	4244	9136
Independent reflections	1708 [$R_{int} = 0.0159$]	4244 [$R_{int} = 0.0000$]	9136 [$R_{int} = 0.000$]
Data/restraints/params	1708/1/211	4244/0/357	9135/0/719
Goodness-of-fit on F^2	1.104	1.044	1.025
$R1$, $wR2$ (all data)	0.0772, 0.2025	0.0681, 0.1301	0.1440, 0.1888
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0599, 0.1753	0.0435, 0.1156	0.0587, 0.1492
Largest difference Peak and hole (e Å^{-3})	0.739 and -0.344	0.309 and -0.250	0.756 and -0.403

($M_I = -1/2$ line) standard at $g = 1.9860$. Concentrations of the paramagnetic compounds were determined by double integration of the first derivative spectra. A variable temperature unit STT-3 was used for the measurement in the range 102–296 K. UV–NIR spectra were registered in the range 280–2000 nm on a Varian Cary 17D spectrometer using all-sealed quartz cuvettes (Hellma).

2.2. Chemicals

Compounds $(C_5H_5)_2Ti(bipy)$ (**1**), $(C_5HMe_4)_2Ti(bipy)$ (**2**), and $(C_5Me_5)_2Ti(bipy)$ (**3**) were recently prepared by reacting titanocene-bis(trimethylsilyl)acetylene complexes $(C_5H_{5-n}Me_n)_2Ti[\eta^2\text{-}C_2(SiMe_3)_2]$ ($n = 0$, 4, and 5) [9] with 2,2′-bipyridyl [7]. Authentic, well-characterised crystalline samples of **1**–**3** were dissolved in toluene. The solutions were used for UV–NIR and ESR measurements, for obtaining of solid samples by rapid evaporation in ESR sample tubes, and for obtaining single crystals from saturated solutions by slow cooling. Toluene was purified by conventional methods, dried by refluxing over $LiAlH_4$ and stored as solutions of 'dimeric titanocene' $(C_{10}H_8)[(C_5H_5)Ti(\mu\text{-}H)]_2$ [10].

2.3. X-ray crystal analyses of *1*–*3*

Crystal fragments of **1**–**3** were mounted onto Lindemann glass capillaries under purified nitrogen and sealed with wax. The structure measurements were carried out on an Enraf–Nonius CAD4 diffractometer at ambient temperature using graphite-monochromated Mo–K_α radiation. Data were collected using $\theta/2\theta$ scans. The phase problem was solved by direct methods SIR-92 [11], and the refinement was carried out by the SHELXL-93 program [12].

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1**

Atom	x	y	z	U_{eq}^a
Ti(1)	6850(1)	1154(1)	405(2)	47(1)
N(1)	7938(4)	1451(2)	1483(9)	59(2)
N(2)	6496(3)	1814(2)	1580(8)	52(1)
C(10)	6491(7)	892(4)	−2339(12)	80(3)
C(11)	6182(6)	1353(3)	−2153(11)	75(2)
C(12)	6808(7)	1662(3)	−2058(12)	82(3)
C(13)	7526(7)	1414(4)	−2153(12)	86(3)
C(14)	7337(7)	928(3)	−2333(11)	80(3)
C(20)	6477(8)	331(3)	929(14)	92(3)
C(21)	5843(6)	593(4)	1498(15)	90(3)
C(22)	6122(9)	863(4)	2897(15)	94(3)
C(23)	6882(9)	785(5)	3175(17)	104(5)
C(24)	7138(7)	422(4)	1913(22)	113(5)
C(100)	8685(5)	1285(3)	1281(15)	77(2)
C(101)	9290(5)	1421(4)	2482(19)	101(4)
C(102)	9125(6)	1711(4)	3878(16)	88(3)
C(103)	8408(5)	1867(3)	4026(12)	73(2)
C(104)	7794(4)	1767(2)	2801(9)	56(2)
C(105)	7014(4)	1977(2)	2845(9)	53(2)
C(106)	6744(5)	2337(3)	4035(12)	70(2)
C(107)	6036(5)	2534(3)	3874(12)	77(2)
C(108)	5527(5)	2389(3)	2530(14)	79(2)
C(109)	5767(4)	2038(2)	1439(11)	61(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table 3
Atom coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for the two molecules of **2**[a]

Atom	x	y	z	U_{eq}
Ti(1)	5163(1)	2500	12640(1)	32(1)
N(1)	4576(1)	1747(1)	11769(1)	41(1)
C(10)	6450(2)	2500	13048(3)	42(1)
C(11)	6363(2)	1834(2)	12527(2)	45(1)
C(12)	6221(1)	2088(2)	11673(2)	49(1)
C(13)	6541(2)	1018(2)	12830(3)	80(1)
C(14)	6185(2)	1591(3)	10862(3)	95(2)
C(20)	5116(2)	2500	14172(3)	60(1)
C(21)	4720(2)	3158(2)	13927(2)	57(1)
C(22)	4039(2)	2905(2)	13540(2)	51(1)
C(23)	4911(4)	3993(3)	14146(4)	125(2)
C(24)	3387(2)	3408(4)	13274(3)	106(2)
C(100)	4646(2)	960(2)	11696(2)	57(1)
C(101)	4152(2)	506(2)	11248(3)	76(1)
C(102)	3517(2)	845(3)	10870(2)	72(1)
C(103)	03426(2)	1620(2)	10916(2)	60(1)
C(104)	3971(1)	2089(2)	11343(2)	43(1)
Ti(2)	3379(1)	2500	7213(1)	30(1)
N(2)	2843(1)	1742(1)	8141(1)	34(1)
C(30)	4643(2)	2500	6705(3)	42(1)
C(31)	4582(1)	1833(2)	7229(2)	46(1)
C(32)	4484(1)	2093(2)	8094(2)	52(1)
C(33)	4744(2)	1017(2)	6943(4)	84(1)
C(34)	4480(2)	1594(4)	8904(3)	107(2)
C(40)	3232(2)	2500	5680(2)	46(1)
C(41)	2850(2)	1835(2)	5978(2)	44(1)
C(42)	2200(1)	2092(2)	6430(2)	43(1)
C(43)	3017(3)	1001(2)	5735(3)	77(1)
C(44)	1567(2)	1583(3)	6756(2)	73(1)
C(200)	2905(2)	960(2)	8188(2)	46(1)
C(201)	2450(2)	495(2)	8683(2)	55(1)
C(202)	1864(2)	841(2)	9162(2)	57(1)
C(203)	1787(2)	1621(2)	9137(2)	54(1)
C(204)	2295(1)	2089(2)	8649(2)	37(1)

[a] Symmetry transformations used to generate equivalent atoms [N(1′), C(11′),... C(101′)...]: $x, -y+1/2, z$.

Compound **1** was measured in a monoclinic cell; this was transformed to orthorhombic after the data reduction. Compound **3** showed a disorder of one of the C_5Me_5 ligands in one of the two inequivalent molecules (**3b**) over two sites. Observable maxima were found on the Fourier map, half-way between the methyl groups. The refinement performed over these two sites for Me carbon atoms gave an occupancy ratio of about 10:1. The attempt to treat this site disorder for the whole ligand failed as the lowering of the occupancy factor for the main cyclopentadienyl ring carbon atoms resulted in their anisotropic displacement parameters going non-

Table 4
Atom coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for the two molecules of **3**

Atom	x	y	z	U_{eq}
Ti(1)	7793(1)	5037(1)	11054(1)	35(1)
C(10)	6837(3)	5245(2)	11909(2)	60(1)
C(11)	7568(4)	5179(2)	12193(2)	59(1)
C(12)	8086(3)	5513(2)	11975(3)	66(2)
C(13)	7642(5)	5773(2)	11513(3)	75(2)
C(14)	6867(4)	5597(2)	11509(2)	67(2)
C(15)	6072(5)	4991(4)	12092(6)	144(4)
C(16)	7761(8)	4864(3)	12747(3)	133(4)
C(17)	8845(5)	5654(4)	12302(5)	170(5)
C(18)	7920(10)	6199(2)	11216(5)	188(6)
C(19)	6139(6)	5797(4)	11183(4)	162(5)
C(20)	8691(3)	4435(2)	10675(3)	64(2)
C(21)	9106(3)	4685(2)	11102(3)	71(2)
C(22)	9213(3)	5111(2)	10850(3)	73(2)
C(23)	8821(3)	5123(2)	10242(3)	62(2)
C(24)	8495(3)	4691(2)	10147(2)	57(1)
C(25)	8559(6)	3928(2)	10704(6)	130(3)
C(26)	9514(6)	4514(5)	11713(4)	154(4)
C(27)	9815(4)	5465(4)	11050(6)	154(5)
C(28)	8876(6)	5487(3)	9744(5)	135(4)
C(29)	8087(4)	4522(3)	9546(4)	104(3)
N(1)	6926(2)	5123(1)	10291(2)	40(1)
N(2)	7011(2)	4462(1)	11099(2)	42(1)
C(100)	6907(3)	5462(2)	9869(2)	51(1)
C(101)	6398(4)	5495(2)	9355(2)	62(1)
C(102)	5859(3)	5147(2)	9255(3)	64(2)
C(103)	5842(3)	4798(2)	9675(2)	55(1)
C(104)	6368(2)	4784(1)	10203(2)	39(1)
C(105)	6395(3)	4436(1)	10658(2)	42(1)
C(106)	5838(3)	4079(2)	10698(3)	60(1)
C(107)	5919(4)	3755(2)	11140(3)	69(2)
C(108)	6564(4)	3774(2)	11570(3)	68(2)
C(109)	7067(3)	4130(2)	11532(2)	53(1)
Ti(2)	6916(1)	2422(1)	8617(1)	34(1)
C(30)	6304(6)	3033(2)	9221(4)	95(3)
C(31)	5693(4)	2790(3)	8976(3)	89(2)
C(32)	5691(4)	2388(3)	9246(4)	88(2)
C(33)	6307(5)	2363(2)	9658(3)	84(2)
C(34)	6701(3)	2761(3)	9651(3)	89(2)
C(35)	6413(14)	3520(3)	9117(9)	338(15)
C(36)	5012(8)	2959(7)	8579(5)	308(13)
C(37)	4998(9)	2053(6)	9237(9)	270(11)
C(38)	6444(12)	1998(5)	10132(6)	326(14)
C(39)	7359(6)	2909(7)	10076(6)	306(13)
C(40)	7357(3)	2233(2)	7506(2)	51(1)
C(41)	6534(3)	2318(2)	7504(2)	57(1)
C(42)	6158(3)	1976(2)	7860(2)	55(1)
C(43)	6761(3)	1698(1)	8115(2)	49(1)
C(44)	7501(3)	1857(2)	7880(2)	48(1)
C(45)	7992(5)	2474(3)	7120(3)	94(2)
C(46)	6106(6)	2652(3)	7083(3)	107(3)
C(47)	5288(4)	1841(3)	7804(4)	113(3)
C(48)	6628(5)	1259(2)	8451(3)	86(2)
C(49)	8292(3)	1621(3)	7933(3)	84(2)
N(3)	8042(2)	2242(1)	9072(2)	41(1)
N(4)	7744(2)	2955(1)	8383(2)	42(1)
C(200)	8182(3)	1870(2)	9417(2)	55(1)
C(201)	8898(4)	1759(2)	9683(3)	64(2)
C(202)	9547(3)	2044(2)	9603(2)	61(1)
C(203)	9437(3)	2419(2)	9249(3)	55(1)
C(204)	8679(2)	2529(1)	8981(2)	41(1)
C(205)	8519(3)	2918(1)	8618(2)	43(1)
C(206)	9090(3)	3255(2)	8479(3)	65(2)
C(207)	8878(4)	3613(2)	8119(3)	77(2)
C(208)	8102(4)	3651(2)	7891(3)	69(2)
C(209)	7575(3)	3318(2)	8031(3)	57(1)

positive definite. The inspection of the Fourier section drawn through the planes of the cyclopentadienyl rings revealed that the ghost ring carbon atoms cannot be localised, since they are smeared by large anisotropic thermal parameters of the main ring carbon atoms. Due to the poor data quality the refinement of the site disorder was then abandoned.

Hydrogen atoms residing on the cyclopentadienyl methyl groups were refined as riding atoms with an effective distance of 0.96 Å. Hydrogen atoms of the bipyridyl and cyclopentadienyl ligands were localised from difference Fourier maps except for **1**, where these were refined as riding atoms.

Crystal data are summarised in Table 1, atomic coordinates and isotropic thermal parameters of **1** and **2** and **3** are given in Table 2, Tables 3 and 4.

3. Results and discussion

3.1. Crystal structures of the $(C_5H_{5-n}Me_n)_2Ti(bipy)$ [$n = 0$ (**1**), 4 (**2**) and 5 (**3**)] complexes

The X-ray diffraction analyses revealed that the Ti atom is pseudotetrahedrally coordinated by two cyclopentadienyl ligands and by two nitrogen atoms of the bpy ligand in all the compounds. This structural similarity is crystallographically expressed in orthorhombic symmetry of space groups (Table 1). Compound **1** showed the cell parameters to be virtually equal with those reported in a preliminary study [8]. Its molecular structure with atom numbering scheme is shown in Fig. 1. Compounds **2** and **3** contain two inequivalent

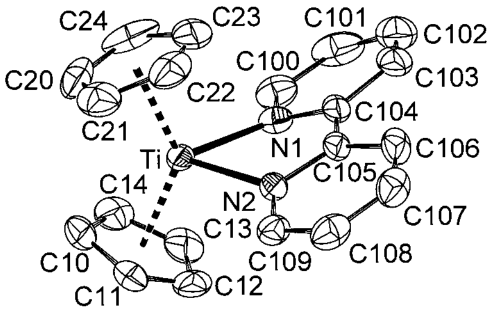

Fig. 1. PLATON drawing of $(C_5H_5)_2Ti(bipy)$ (**1**) with 30% probability ellipsoids and atom numbering scheme.

molecules in the unit cell (denoted **2a** and **2b**, and **3a** and **3b**). PLATON [13] drawings of **2a** and **3a** with atom numbering schemes are shown in Figs. 2 and 3, respectively. Selected geometric parameters for **1**, **2a**, **2b**, **3a**, and **3b** are listed in Table 5. These data show that the congener molecules differ only slightly. The molecules of **2** are symmetrical with respect to the plane which contains the Ti atom, centroids (CE) of the C_5HMe_4 rings and their carbons atoms bearing one proton each, and bisects the bpy ligand. The eclipsed conformation of the C_5HMe_4 ligands in a titanocene species is observed for the first time (cf. Ref. [14]). The cyclopentadienyl rings are slightly staggered in **1** and regularly staggered in **3**. The methyl groups in **2** are bent away from the ring plane farther away from the Ti atom. The largest deviations from the CE1 ring were found for the C13 and C13′ atoms (average for two molecules, 0.22 Å) and from CE2 ring for the C24 and C24′ atoms (average for two molecules, 0.17 Å). The latter deviation may indicate the steric hindrance between the C_5HMe_4 ligand and the bent bpy ligand (vide infra). In **3**, the most deviated Me groups are those close to the top of the dihedral angle (ϕ) contained by the least squares planes of the C_5Me_5 rings (average deviation, 0.40 Å). This is a common effect of the steric congestion in the area of close contacts of the C_5Me_5 ligands. The average Ti–CE distance moves from 2.08(2) Å for **1** to 2.12(1) Å for **2** and to 2.14(2) Å for **3**. A similar regular effect is not observed for the average Ti–N bond lengths which are the same for **1** (2.14(2) Å), **2** (2.14(1) Å), and **3** (2.17(2) Å) within the error. This is compatible with the values of zero-field splitting constants showing only negligibly lower value for **3** ($D = 0.0395$ cm^{-1}) compared to that of **2** ($D = 0.0405$ cm^{-1}) [7]. The differences in the bond lengths of the bpy ligands for all the compounds do not exceed three-fold values of errors (esds). A slightly smaller N–Ti–N angle in **3** apparently follows from the above mentioned longer Ti–N distance (cf. Table 5). The deviations of atoms from the least-squares plane of bpy ligand are well below 0.01 Å for **3** and slightly above this value in **1** and **2**.

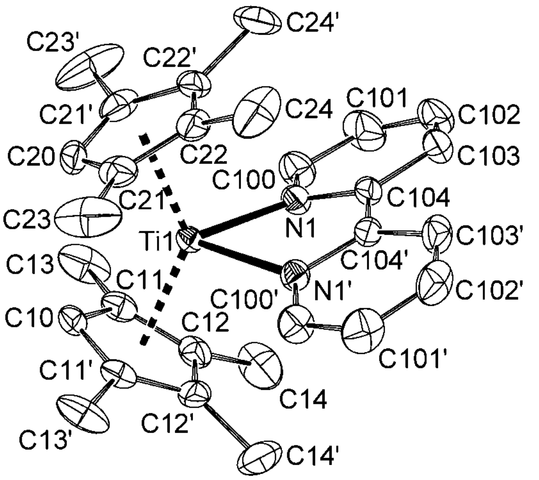

Fig. 2. PLATON drawing of $(C_5HMe_4)_2Ti(bpy)$ (**2a**) with 30% probability ellipsoids and atom numbering scheme. Molecule **2b** is numbered by Ti(2), N(2), C(30)–C(34), C(40)–C(44), and C(200)–C(204).

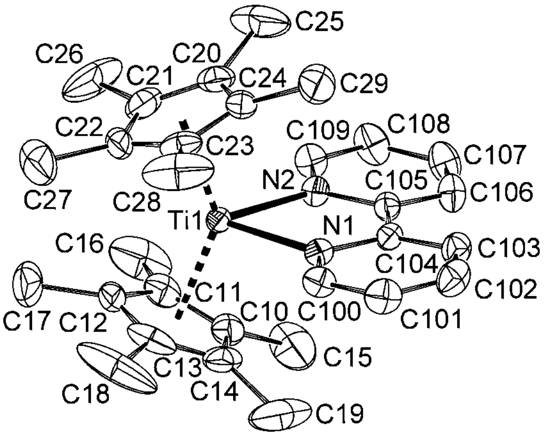

Fig. 3. PLATON drawing of $(C_5Me_5)_2Ti(bpy)$ (**3a**) with 30% probability ellipsoids and atom numbering scheme. Molecule **3b** is numbered by Ti(2), N(3), N(4), C(30)–C(39), C(40)–C(49) and C(200)–C(209).

A substantial difference in the structures of **1**–**3** occurs in the placement of bpy ligand with respect to the plane defined by the Ti and two N atoms (see Fig. 4). In **3**, the least squares plane of the bpy ligand is virtually identical with the above reference plane which bisects the CE–Ti–CE angle. This arrangement has also been found in the Ti(IV) and Ti(II) complexes [bis(cyclopentadienyl)(bpy)titanium(IV)]$^{2+}$[trifluoro-methanesulfonate]$_2^-$ [15] and bis(2,6-diisopropylphenoxy)-(bpy)$_2$titanium(II) [16]. In **1** and **2**, the bpy plane declined from the reference plane by 23.2(4)° for **1**, and on average by 18.7(2)° for **2**. The drawing of angles calculated using the SHEXL-93 program is shown in Fig. 4 and their values for **1**–**3** are listed in Table 6. The asymmetric position of the bpy ligand induces a considerable asymmetry in the titanocene moiety. The CE2 ligands of **1** and **2a** and the CE4 ligand of **2b** are in a close contact with the bpy ligand as their planes approach each other under the angle (γ_2) of 3.5° for **1** and on average 6.2° for **2** (see Fig. 4 and Table 6). In **2**, the C_5HMe_4 ligands are inclined each to other by the proton-bearing carbon atoms so that the angle between the Ti–CE line and the least squares plane of the C_5HMe_4 ligand is 86.2° for CE1 ring plane and 85.0° for the CE2 ring plane. This facilitates reaching the bent position of the bpy ligand between otherwise methyl-substituted cyclopentadienyl rings. In **1** and **3**, the least-squares planes are perpendicular to the Ti–CE vectors within 1°.

Table 5
Selected bond lengths [Å] and angles (deg) for **1**, **2** and **3**

	1	**2a**	**2b**	**3a**	**3b**
Bond distances					
Ti–CE(1)	2.052(10)	2.120(2)	2.115(2)	2.144(6)	2.134(8)
Ti–CE(2)	2.104(12)	2.129(2)	2.119(2)	2.131(6)	2.140(5)
Ti–N(1)	2.159(6)	2.129(2)	2.150(2)	2.167(3)	2.172(3)
Ti–N(2)	2.127(5)	2.129(2)	2.150(2)	2.161(3)	2.165(3)
Bond angles					
CE(1)–Ti–CE(2)	135.6(4)	136.5(1)	137.2(1)	140.8(2)	139.5(2)
N(1)–Ti–N(2)	74.8(2)	75.09(12)	74.82(11)	74.00(13)	74.34(13)
C(100)–N(1)–Ti	127.2(6)	127.7(2)	127.1(2)	126.0(3)	126.2(3)
C(104)–N(1)–Ti	112.9(5)	114.3(2)	114.7(2)	117.2(3)	116.8(3)
C(109)–N(2)–Ti	126.9(5)	–	–	125.1(3)	125.8(3)
C(105)–N(2)–Ti	114.5(5)	–	–	117.6(3)	117.1(3)

Table 6
Dihedral angles between molecular planes in **1**, **2** and **3**

Planes (denotation)[a]	**1**	**2a**	**2b**	**3a**	**3b**
I II (ϕ)	46.0(4)	52.3(2)	50.6(2)	42.6(3)	42.5(3)
I III (α_1)	25.8(4)	27.0(2)	26.2(2)	21.2(3)	21.1(3)
II III (α_2)	20.3(4)	25.4(2)	24.4(2)	21.4(3)	21.4(3)
III IV (β)	23.2(4)	20.0(2)	17.5(2)	2.5(3)	1.1(3)
I IV (γ_1)	49.0(4)	46.9(2)	43.6(2)	22.6(3)	22.1(3)
II IV (γ_2)	3.5(5)	5.4(2)	7.0(2)	20.3(3)	20.4(3)

[a] The angles are depicted in Fig. 4.

3.2. Temperature dependence of ESR signal intensities

Solid samples of compounds **2** and **3** obtained by rapid evaporation of toluene solutions give ESR single lines at $g = 1.997$ with $\Delta H_{pp} = 3.7$ mT for **2** and 4.5 mT for **3** at 296 K. The intensity of the integrated signal of **3** increases with decreasing temperature in the range 296–102 K. In contrast, the signal intensity of **2** grows from 296 K to 229 K and then decreases. Intensity vs. temperature plots for the both samples are shown in Fig. 5, curves 1 and 2, respectively. At the liquid nitrogen temperature (77 K), a continuing increase in the signal intensity of **3** and a decrease in the signal intensity of **2** were established using the intensity of an Mn^{2+} standard situated outside the Dewar vessel as a reference. These intensity values are not, however, compatible with the values obtained using a variable temperature Dewar vessel and cannot be used for extension curves 1 and 2. In the range of temperatures 176–102 K, the intensities of ESR spectra of the triplet state of **2** in toluene glass were also measured using the integration over the range 275–395 mT (Fig. 5, curve 3). At temperatures near the melting point of toluene, the intensities were lower compared to those of the solid sample plot. This can be caused by the diminishing of the spectrum width due to an increased mobility in a soft matrix.

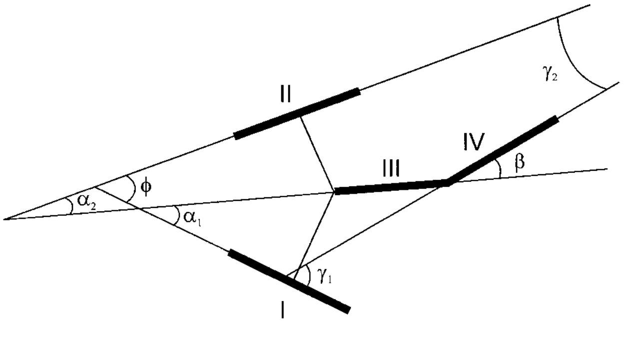

Fig. 4. Scheme of planes and dihedral angles between them for compounds **1**–**3**: I-least squares plane of the CE1 (and CE3) ring; II-least squares plane of the CE2 (and CE4) ring; III-Ti, N, N; IV-least squares plane of bpy).

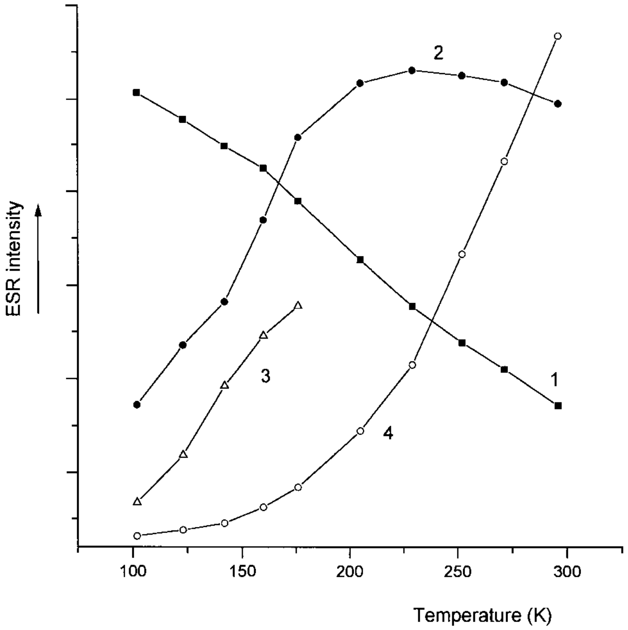

Fig. 5. Temperature dependences of the ESR signal intensity for compounds **2** and **3**. Curve 1-solid sample of **3;** curve 2-solid sample of 2; curve 3-**2** in toluene glass; curve 4-crystalline **2**. The ESR intensity is in arbitrary units which are compatible within the particular dependence plot only.

A surprising temperature dependence occurred for the sample of well developed crystalline **2**. In this case, the intensity was smoothly decreasing already from 296 K (Fig. 5, curve 4). The reason for the different behaviour of this and the solid, probably largely amorphous sample is not clear. It is not due to the presence of a Ti^{3+} mononuclear impurity as the solid sample was later dissolved in toluene and showed the same amount of the impurity as observed in the previously published spectrum [7] (ca. 0.7% at 142 K as calculated from areas under the integrated record). We suggest that in well-developed crystals the triplet state is populated with a higher activation energy than in a poorly ordered solid.

3.3. Implications for the relationship between the structure and the multiplicity of the electronic state

The X-ray and ESR results justify the conclusion by McPherson et al. [8] that the orientation of the bpy ligand with respect to the titanocene moiety is associated with the prevailing population of the electronic state. Based on the temperature dependence of the ESR signal intensity showing a steady growth with decreasing temperature and on a six-fold higher intensity of the triplet state spectrum of **3** in toluene glass compared to an equally concentrated glass of **2** [7], we can conclude that compound **3** is in a triplet state over the applied temperature range. Since the change of the bpy position seems to be precluded by steric requirements, the triplet state can be considered to be a ground state. On the other hand, lower populations of triplet states in **1** and **2** and a decrease in intensities of their ESR spectra with lowering of temperature indicate that these compounds have a ground singlet state [8]. In spite of an induced steric congestion between the bpy and cyclopentadienyl ligands, the singlet state is lower in energy than the triplet state with a released steric hindrance. This is understandable in a view of the unpaired electron delocalised over the bpy radical anion in an MO directed perpendicularly to the plane of bpy ligand. In **3**, the steric hindrance between the bpy and C_5Me_5 ligands is probably dominating in the stabilisation of the ground triplet state. The calculation of energies of both spin states taking into account the steric contributions is a formidable task; the present structural results are indispensable prerequisites.

4. Supplementary material available

Listings of atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. These, together with the lists of observed and calculated structure factors and further details of the structure determination, are available from authors (R.G.).

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