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η^5-Pentabenzylcyclopentadienyl derivatives of titanium (IV), (III), and (II). The crystal structures of $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Bz_5)TiCl_2$ (Bz = benzyl), $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Bz_5)TiCl$, and $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Bz_5)Ti[\eta^2\text{-}(CSiMe_3)_2]$

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Abstract

The reaction of $(\eta^5\text{-}C_5H_5)TiCl_2$ with $K(C_5Bz_5)$ (Bz = benzyl) affords $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Bz_5)TiCl$ (**1**) in a high yield. The oxidation of **1** with AgCl in THF yields $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Bz_5)TiCl_2$ (**2**), whereas the reduction of **1** with Mg in the presence of bis(trimethylsilyl)acetylene gives $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Bz_5)Ti[\eta^2\text{-}(CSiMe_3)_2]$ (**3**). The X-ray analyses of **1**, **2**, **3** revealed, that in **1** two, whereas in **2** and **3** only one, of the Bz substituents are inclined towards the Ti atom. The ESR spectra of **1** in solution and in the glassy state showed that it is monomeric in toluene from 23 to −140°C; however, in 2-methyltetrahydrofuran it coordinates the solvent at low temperature.

Key words: Titanium; π-aromatic ligands; Structure; Cyclopentadienyl

1. Introduction

In spite of increasing interest in bulky cyclopentadienyl transition metal complexes only few η^5-pentabenzylcyclopentadienyl ($\eta^5\text{-}C_5Bz_5$) complexes have been listed in a recent review [1]. The $(\eta^5\text{-}C_5Bz_5)Mn(CO)_3$ [2], $(\eta^5\text{-}C_5Bz_5)Re(CO)_3$ [2], and $(\eta^5\text{-}C_5Bz_5)Co(CO)_2$ [3] complexes were prepared in a redox reaction of pentabenzylcyclopentadiene (C_5Bz_5H) with dinuclear carbonyls. The $(\eta^5\text{-}C_5Bz_5)_2Fe$ [2,4], $(\eta^5\text{-}C_5Bz_5)(\eta^5\text{-}C_5Me_5)Fe$ [2], $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Bz_5)Fe$ [2], $(\eta^5\text{-}C_5Bz_5)Rh(CO)_2$ [3], and $(\eta^5\text{-}C_5Bz_5)Au(PPh_3)$ [5] were obtained by the reaction of $(C_5Bz_5)Li$ with the appropriate chlorides or acetylacetonates. The first C_5Bz_5 titanium complex $(\eta^5\text{-}C_5Bz_5)Ti^{III}(AlCl_4)_2$ has recently been obtained by the redox reaction of C_5Bz_5H with $(\eta^6\text{-}C_6H_6)Ti^{II}(AlCl_4)_2$ [6]. Here we describe the synthesis and crystal structures of (cyclopentadienyl)(pentabenzylcyclopentadienyl)titanium(IV), (III), and (II) derivatives $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Bz_5)TiCl_2$ (**2**), $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Bz_5)TiCl$ (**1**), and $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Bz_5)Ti[\eta^2\text{-}(CSiMe_3)_2]$ (**3**).

2. Experimental details

2.1. General

Manipulation with all reagents, synthesis, and spectroscopic measurements were carried out under vacuum using all-sealed devices equipped with breakable seals. The solvents, toluene, hexane, THF and 2-methyltetrahydrofuran (MTHF) were purified by conventional methods and dried by refluxing over $LiAlH_4$ and stored as solutions of dimeric titanocene ($\eta^5:\eta^5$-

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$C_{10}H_8$)-[(η^5-C_5H_5)Ti(μ-H)]$_2$ [7]. 1,2,3,4,5-Pentabenzylcyclopentadiene was prepared by an improved procedure [6], based on the method described by Hirsch and Bailey [8] and Chambers et al. [3]. (η^5-C_5H_5)$TiCl_3$ was obtained by heating of equimolar amounts of (η^5-C_5H_5)$_2TiCl_2$ and $TiCl_4$ in m-xylene to 140°C for 3 h. After evaporation of the solvent and traces of $TiCl_4$ the residue was twice sublimed in vacuo to give the pure compound. Butyl lithium (BuLi) 1.6 M in hexane (Chemetall, Frankfurt) was degassed and distributed into ampoules under vacuum. The potassium hydride suspension in paraffin oil (Fluka) was degassed and the oil was replaced by hexane. Bis(trimethylsilyl)acetylene (BTMSA) (Fluka) was degassed and distilled in vacuo. Silver chloride (Fluka) and magnesium turnings (Fluka, purum for Grignard reactions) were used as obtained.

2.2. *Methods*

Mass spectra were obtained on a JEOL JMS D-100 spectrometer at 75 eV using direct inlet with programmed heating up to 250°C. The capillaries, containing the samples under vacuum, were opened and inserted into the direct inlet under argon. ^1H and ^{13}C NMR spectra were measured on a Varian VXR-400 spectrometer (400 MHz and 100 MHz, respectively) in C_6D_6 at 25°C. Chemical shifts (given in the δ-scale) were referenced to the solvent signal (δ_H 7.15 ppm, δ_C 128.00 ppm). ^1H assignments are based on the displayed coupling pattern and long-range coupling of the ortho-protons to the benzylic methylene (a cross-peak in the delayed-COSY experiment). The multiplicity of carbon signals was determined from APT and proton-coupled ^{13}C NMR spectra. ^{13}C assignment stems from the HETCOR results and examination of proton-coupled ^{13}C NMR spectra. The EPR spectra in X-band were measured on an ERS-220 spectrometer (ZWG, Berlin) equipped with a proton magnetometer and a variable temperature unit. The solutions in toluene or MTHF were measured at room temperature and in the glassy state at −140°C. UV-Vis spectra were recorded in the range 270–2000 nm on a Varian Cary 17D spectrometer using all-sealed quartz cuvettes (Hellma). Infrared spectra were obtained on a Mattson Galaxy 2020 spectrometer. The samples in KBr pellets were prepared in a glovebox (Braun) in an atmosphere of purified nitrogen and were measured in a special cell protecting them against the oxidation by air.

2.3. *Synthesis of* (η^5-C_5H_5)$TiCl_2$

(η^5-C_5H_5)$TiCl_3$ (0.88 g, 4 mmol) was reduced in 30 ml THF with 0.2 g of Zn turnings for three hours [9,10]. The resulting blue solution was separated from unreacted Zn. THF was evaporated at room temperature and subsequently at 100°C. The sky blue crystalline solid of (η^5-C_5H_5)$TiCl_2$ · 1.5THF turned to a mauve powder of [(η^5-C_5H_5)$TiCl_2$]$_n$ [9]. The mauve residue was washed eight times with 5 ml of diethyl ether to remove $ZnCl_2$ and was dried in vacuo. The yield of solid [(η^5-C_5H_5)$TiCl_2$]$_n$ was 0.64 ± 0.05 g, ca. 3.5 mmol. The etheral extracts contained a small amount of product.

2.4. *Synthesis of* (C_5Bz_5)K

An excess of dry KH (0.4 g) was added to a solution of colourless 1,2,3,4,5-pentabenzylcyclopentadiene (2.07 g, 4 mmol) in 40 ml of THF. The suspension was stirred until the hydrogen evolution had ceased and the reaction mixture turned deep red. The red solution was filtered from the excess of KH and used without further purification. The reaction was apparently nearly quantitative.

2.5. *Synthesis of* (^{5}-C_5H_5)(^{5}-C_5Bz_5)TiCl (*1*)

The solution of (C_5Bz_5)K (approx. 3.9 mmol in 40 ml of THF) was added to solid mauve (η^5-C_5H_5)$TiCl_2$ (approx. 3.5 mmol, vide supra). The reaction mixture turned immediately deep blue and was stirred overnight. THF was evaporated in vacuo. The dark blue residue was extracted with a toluene/hexane mixture and crystallized from the same solvent (yield 1.5 g, 56% related to (η^5-C_5H_5)$TiCl_3$)).

(η^5-C_5H_5)(η^5-C_5Bz_5)TiCl (**1**): MS m/z (%): M^+ 663 (58.0), 627 (5.5), 599 (9.5), 598 (14.5), 597 (10.5), 536 (17.0), 506 (10.0), 445 (15.5), 416 (10.0), 325 (10.5), 255 (9.0), 241 (6.5), 239 (5.5), 215 (4.5), 181 (5.0), 167 (6.0), 148 (20.5), 129 (7.0), 117 (5.5), 115 (7.5), 105 (5.5), 91 (100), 77 (11.5), 65 (15.5). EPR (toluene, 23°C): $g = 1.9570$, $\Delta H = 1.0$ mT; (toluene, frozen glass at −140°C): $g_1 = 1.9977$, $g_2 = 1.9805$, $g'_3 = 1.8919$, $g''_3 = 1.8872$, $g'_{av} = 1.9567$, $g''_{av} = 1.9551$. (MTHF, 23°C): minor signal $g = 1.9793$, $\Delta H = 0.5$ mT, a(Ti) = 1.17 mT, major signal $g = 1.9570$, $\Delta H = 1.0$ mT; (MTHF, −38°C): major signal $g = 1.9799$, $\Delta H = 0.7$ mT, a(Ti) = 1.17 mT, minor signal at $g = 1.957$ is poorly discernible; (MTHF, frozen glass at −140°C): $g_1 = 2.0003$, $g_2 = 1.9816$, $g_3 = 1.9595$, $g_{av} = 1.9805$. UV-Vis (toluene, 25°C; ⟨,⟩ relative intensity): 350sh > 390sh > 557 > 660sh nm; (MTHF, 25°C): 350sh > 390sh > 555 > 660sh nm; (MTHF, −20°C): 570sh < 700 very broad (extended to 1100) nm.

2.6. *Synthesis of* (η^5-C_5H_5)(η^5-C_5Bz_5)$TiCl_2$ (*2*)

Compound **1** (0.2 ± 0.05 g, 1.1 mmol) was dissolved in 30 ml THF and AgCl (0.5 g) was added. After stirring overnight the blue colour of **1** turned to a light red colour of **2**. THF was evaporated in vacuo and the residue was extracted with hot hexane (50 ml). Red needle crystals (0.2 ± 0.05 g) were obtained by slow cooling of the concentrated solution. The mother liquor was only slightly yellow. Caution: compound **2** is photosensitive. Its solutions should be handled in the dark. $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Bz_5)TiCl_2$ (**2**). MS m/z (%): 663 (43.0) $[M-Cl]^+$, 633 (3.3) $[M\text{-}(C_5H_5)]^+$, 627 (2.3), 598 (16.5), 597 (15.0) $[M\text{-}Cl\text{-}(C_5H_5)]^+$, 596 (17.5), 536 (9.3), 516 (2.5) $[C_5Bz_5H]^+$, 515 (2.8), 514 (5.8), 506 (7.5), 445 (8.8), 416 (7.5), 415 (7.5), 269 (4.3), 255 (13.0), 241 (9.8), 215 (5.8), 181 (5.5), 167 (10.5), 165 (8.3), 148 (14.0), 115 (5.0), 91 (100), 65 (11.0). ^1H NMR (C_6D_6, 25°C): δ 3.895 (s, 10H, CH_2); 6.131 (s, 5H, Cp); 6.630 (mt, 10H, ortho-); 7.197 (mt, 15H, meta- and para-). ^{13}C NMR (C_6D_6, 25°C): δ 35.36 (t, 5C, CH_2); 120.76 (d, 5C, Cp); 126.39 (d, 5C, para-); 128.19 (d, 10C, meta-) 129.65 (d, 10C, ortho-); 132.94 (s, 5C, Bz_5C_5); 138.73 (s, 5C, ipso-). IR (KBr-pellet, cm^{-1} (transmission, %)): 3104 (63), 3084 (62), 3061 (58), 3028 (57), 2949 (58), 2924 (58), 2870 (62), 2855 (62), 1601 (53), 1589 (58), 1495 (43), 1476 (57), 1451 (42), 1099 (54), 1076 (50), 1030 (46), 1018 (49), 984 (53), 826 (42), 756 (54), 737 (37), 698 (35), 482 (51), 463 (52), 426 (55).

2.7. Synthesis of $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Bz_5)Ti[\eta^2\text{-}(CSiMe_3)_2]$ (**3**)

Compound **1** (0.3 ± 0.05 g, 1.6 mmol) was dissolved in a solution of (0.31 ± 0.05 g, 1.8 mmol) BTMSA in 10 ml of THF. This solution was poured onto Mg turnings (0.1 g). After stirring overnight the blue colour of **1** changed to the yellow colour of **3**. The solvent was evaporated in vacuo and the residue was extracted with hexane. Yellow crystals of **3** (0.3 ± 0.05 g, ca. 80%) were obtained by cooling of the concentrated hexane solution. These crystals were used for X-ray analysis, IR measurements and for the preparation of solutions for NMR and ESR measurements.

$(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Bz_5)Ti[\eta^2\text{-}(CSiMe_3)_2]$ (**3**). MS thermal decomposition m/z, (%) [100–150°C], $[BTMSA]^+$ 170 (15), 155 (100); [180°C] 777 (4), 766 (13), $[(C_5H_5)(C_5Bz_5)TiH]^+$ 627 (100), 536 (47), 514 (21), 445 (83), 365 (6), 354 (17), 331(3), 300 (4), 265 (5), 253 (6), 241 (6), 204 (6), 190 (9), 167 (4), 165 (4), 113 (19), 91 (62), 65 (8). ^1H NMR (C_6D_6, 25°C): δ 0.062 (s, 18H, $SiMe_3$); 3.287 (s, 10H, CH_2); 6.336 (s, 5H, Cp); 6.782 (mt, 10H, ortho-); 6.908-6.989 (mt, 15H, meta- and para-). ^{13}C NMR (C_6D_6, 25°C): δ 2.58 (q, 6C, $SiMe_3$); 34.36 (t, 5C, CH_2); 116.86 (d, 5C, Cp); 126.08 (d, 5C, para-); 127.10 (s, 5C, Bz_5C_5); 128.26 (d, 10C, meta-); 129.21 (d, 10C, ortho-); 140.43 (s, 5C, ipso-); 244.79 (s, 2C, $C\equiv C$). ^{13}C NMR (C_6D_6, 25°C) coupled: δ (J, Hz) 2.58 Qqq (118.7, 2.1, 2.1); 34.36 Tt (126.O, 4.2); 116.86 Dtt (171.5, 6.7, 6.7); 126.08 Dt (159.5, 7.4); 127.10 tt (6.7, 4.2); 128.26 Dd (159.8, 7.2); 129.21 Ddt (157.8, 11.0, 4.7); 140.43 tt (6.8, 6.8); 244.79 qqq (1.8, 1.8, 1.8). The NMR spectra are compatible with the proposed structure. The ^1H assignments are based on the displayed coupling pattern and long-range coupling of the ortho-protons to the benzylic methylene (a cross-peak in the delayed COSY experiment). The multiplicity of the carbon signals was determined from APT and proton-coupled ^{13}C NMR spectra. ^{13}C assignments stem

TABLE 1. Crystallografic data for **1**, **2** and **3**

	1	**2**	**3**
Crystal data			
Chem. formula	$C_{45}H_{40}ClTi$	$C_{45}H_{40}Cl_2Ti \cdot 1/2(C_6H_{14})$	$C_{53}H_{58}Si_2Ti$
Mol. wt.	664.14	699.60 + 43.09	799.09
Crystal system	orthorhombic	monoclinic	triclinic
Space group	$Pna2_1$	$P2_1/n$	$P\bar{1}$
a (Å)	25.251(5)	13.640(4)	12.458(7)
b (Å)	8.439(1)	25.004(6)	12.955(7)
c (Å)	16.706(4)	12.343(5)	15.783(7)
α (°)			94.07(5)
β (°)		106.10(2)	99.52(4)
γ (°)			112.53(4)
Z	4	4	2
D_{calc} (g cm^{-3})	1.239	1.220	1.156
μ (MoK_α) (cm^{-1})	3.02	3.30	2.32
Approx. crystal dimensions (mm^3)	0.3 · 0.35 · 0.6	0.3 · 0.5 · 0.7	0.3 · 0.6 · 0.7
Colour	blue	red	yellow
Data collection and refinement			
$2\theta_{max}$ (°)	50	50	46
Unique observed reflections (total)	6091	6765	5993
$F_0 > 1\sigma(F_0)$	5795	5992	5221
No. of variables	426	463	509
R	0.063	0.064	0.077
R_W	0.062	0.063	0.076

from the HETCOR results and the examination of proton-coupled ^{13}C NMR spectrum. IR (KBr pellet, cm^{-1} (transmission, %)): 3084 (54), 3061 (48), 3027 (46), 2951 (42), 2926 (49), 2915 (49), 2899 (50), 1616 (48), 1603 (43), 1584 (52), 1495 (36), 1452 (41), 1242 (38), 1076 (46), 1030 (44), 1017 (43), 855 (16), 833 (25), 793 (27), 752 (40), 733 (29), 694 (28), 478 (48), 461 (51), 446 (46), 422 (48).

2.8. *X-ray crystal structure analyses of 1, 2, and 3*

Crystal fragments of **1** and **3** were mounted into Lindemann glass capillaries under purified nitrogen in a glovebox, those of **2** on air. The capillaries were closed with sealing wax. The X-ray measurements were carried out on a Philips PW1100 four circle diffractometer, using graphite monochromated MoKα radiation ($\lambda = 0.71069$ Å) at room temperature. The structures of **1** and **3** were solved by using the statistically weighted tangent formula of Multan90 [11], whereas the structure of **2** was solved by iterative symbolic addition (ISA) [11]. Crystallographic data for **1**, **2** and **3** are summarized in Table 1. The determination of the polarity of the investigated crystal of **1** was attempted after the isotropic refinement using the effect of anomalous dispersion (acentric space group Pna2_1). However, the difference in the R-values for the two coordinate sets was not significant (0.0001) and no difference in the R-values occurred at the end of refinement. The crystals of **2** contained a slightly disordered hexane molecule around the cystallografic centre of inversion. All non hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were included at calculated positions as contributions to F_c. The PC ULM-package [11] was used for all the calculations. The atomic coordinates of **1**, **2** and **3** are given in Tables 2–4. Selected bond distances and angles for **1**, **2** and **3** are listed in Tables 5–7. [12*]

3. Results and discussion

3.1. *Synthesis and properties of 1, 2, and 3*

The synthesis of the C_5Bz_5 titanium compounds follows the well-known methods for obtaining highly methylated titanocene derivatives (Scheme 1). A Ti(III) starting material has been used to avoid fast redox reactions between Ti(IV) and the bulky and electron rich $(C_5Bz_5)^-$ anion. $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Bz_5)TiCl$ (**1**) was obtained from the reaction of $(\eta^5\text{-}C_5H_5)TiCl_2$ with $(C_5Bz_5)K$ in a high yield without apparent byproducts. The air stable complex $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Bz_5)TiCl_2$ (**2**) was prepared nearly quantitatively by oxidation of **1** by AgCl. Caution: the solutions of **2** are very photosensitive towards sunshine. The attempted preparation of **2** by the reaction of equimolar amounts of $(\eta^5\text{-}C_5H_5)TiCl_3$ and $(C_5Bz_5)K$ in THF afforded only $(\eta^5\text{-}C_5H_5)TiCl_2$, the product of the reduction, and other not identified products. The reduction of **1** by Mg metal in the presence of bis(trimethylsilyl)acetylene) afforded the Ti(II) complex $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Bz_5)Ti[\eta^2\text{-}(CSiMe_3)_2]$ (**3**).

TABLE 2. Atomic parameters of **1**

Atom	x	y	z	U_{eq}
Ti(1)	−0.19436(3)	−0.23956(8)	0.0	0.033(1)
Cl(1)	−0.20132(4)	−0.51673(12)	−0.01716(8)	0.049(1)
C(1)	−0.1276(1)	−0.0440(4)	0.0121(2)	0.032(2)
C(11)	−0.1299(2)	0.1069(5)	0.0613(3)	0.041(2)
C(12)	−0.0754(2)	0.1705(5)	0.0828(3)	0.044(3)
C(13)	−0.0322(2)	0.1473(6)	0.0354(4)	0.060(3)
C(14)	0.0165(3)	0.2144(7)	0.0552(5)	0.083(5)
C(15)	0.0219(3)	0.3042(8)	0.1229(5)	0.088(5)
C(16)	−0.0203(3)	0.3262(8)	0.1706(4)	0.087(5)
C(17)	−0.0694(2)	0.2614(6)	0.1515(3)	0.064(3)
C(2)	−0.1387(2)	−0.0596(5)	−0.0703(2)	0.031(2)
C(21)	−0.1605(2)	0.0697(5)	−0.1239(3)	0.039(2)
C(22)	−0.1229(2)	0.1384(5)	−0.1849(3)	0.037(2)
C(23)	−0.1421(2)	0.2568(6)	−0.2345(3)	0.051(3)
C(24)	−0.1104(2)	0.3192(7)	−0.2943(3)	0.069(4)
C(25)	−0.0596(2)	0.2655(8)	−0.3053(4)	0.077(4)
C(26)	−0.0401(2)	0.1471(7)	−0.2558(4)	0.071(4)
C(27)	−0.0718(2)	0.0862(6)	−0.1953(3)	0.050(3)
C(3)	−0.1243(2)	−0.2156(5)	−0.0939(3)	0.034(2)
C(31)	−0.1233(2)	−0.2902(6)	−0.1757(3)	0.046(3)
C(32)	−0.1688(2)	−0.2537(5)	−0.2312(3)	0.045(3)
C(33)	−0.1601(2)	−0.1768(6)	−0.3033(3)	0.055(3)
C(34)	−0.2032(3)	−0.1493(6)	−0.3549(3)	0.067(4)
C(35)	−0.2528(3)	−0.1976(6)	−0.3357(4)	0.065(4)
C(36)	−0.2614(2)	−0.2746(7)	−0.2643(3)	0.065(4)
C(37)	−0.2200(2)	−0.3049(6)	−0.2138(3)	0.051(3)
C(4)	−0.1033(2)	−0.2929(5)	−0.0253(3)	0.033(2)
C(41)	−0.0748(2)	−0.4491(5)	−0.0282(3)	0.043(2)
C(42)	−0.0191(2)	−0.4319(6)	−0.0599(3)	0.047(3)
C(43)	0.0012(3)	−0.5451(7)	−0.1108(4)	0.071(4)
C(44)	0.0527(3)	−0.5344(10)	−0.1381(4)	0.096(5)
C(45)	0.0849(3)	−0.4138(14)	−0.1135(6)	0.124(7)
C(46)	0.0647(3)	−0.2988(13)	−0.0642(6)	0.137(8)
C(47)	0.0136(2)	−0.3096(8)	−0.0356(4)	0.083(4)
C(5)	−0.1066(2)	−0.1891(5)	0.0408(3)	0.033(2)
C(51)	−0.0838(2)	−0.2178(5)	0.1236(3)	0.040(2)
C(52)	−0.1220(2)	−0.2177(5)	0.1935(3)	0.042(2)
C(53)	−0.1199(2)	−0.1010(6)	0.2512(3)	0.056(3)
C(54)	−0.1555(3)	−0.1055(8)	0.3150(3)	0.071(4)
C(55)	−0.1930(3)	−0.2232(9)	0.3213(4)	0.078(5)
C(56)	−0.1957(2)	−0.3392(8)	0.2638(3)	0.070(4)
C(57)	−0.1598(2)	−0.3364(6)	0.2006(3)	0.054(3)
C(6)	−0.2483(2)	−0.0168(6)	0.0195(3)	0.052(3)
C(7)	−0.2726(2)	−0.1113(6)	−0.0389(3)	0.054(3)
C(8)	−0.2881(2)	−0.2542(6)	−0.0017(4)	0.059(3)
C(9)	−0.2724(2)	−0.2466(6)	0.0782(3)	0.054(3)
C(10)	−0.2481(2)	−0.1006(5)	0.0921(3)	0.051(3)

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* Reference number with asterisk indicates a note in the list of references.

TABLE 3. Atomic parameters of **2**

Atom	x	y	z	U_{eg}
Ti(1)	0.48555(4)	0.25727(2)	0.02488(5)	0.036(1)
Cl(1)	0.65153(6)	0.26853(4)	0.14363(7)	0.053(1)
Cl(2)	0.41865(8)	0.32954(4)	0.10440(8)	0.056(1)
C(1)	0.4900(2)	0.1599(1)	0.0525(3)	0.035(2)
C(11)	0.5630(3)	0.1173(1)	0.0338(3)	0.045(2)
C(12)	0.6128(3)	0.1244(1)	−0.0614(3)	0.043(2)
C(13)	0.5748(3)	0.0985(2)	−0.1644(3)	0.054(2)
C(14)	0.6194(3)	0.1058(2)	−0.2515(4)	0.067(3)
C(15)	0.7044(3)	0.1377(2)	−0.2352(4)	0.071(3)
C(16)	0.7450(3)	0.1623(2)	−0.1325(4)	0.065(3)
C(17)	0.6991(3)	0.1560(2)	−0.0463(3)	0.053(2)
C(2)	0.3927(2)	0.1734(1)	−0.0202(2)	0.033(2)
C(21)	0.3436(3)	0.1467(1)	−0.1323(3)	0.040(2)
C(22)	0.3107(2)	0.0896(1)	−0.1176(3)	0.043(2)
C(23)	0.2995(3)	0.0535(2)	−0.2052(3)	0.063(2)
C(24)	0.2677(4)	0.0013(2)	−0.1961(4)	0.080(3)
C(25)	0.2470(3)	−0.0151(2)	−0.0999(5)	0.077(3)
C(26)	0.2585(3)	0.0198(2)	−0.0110(4)	0.074(3)
C(27)	0.2897(3)	0.0718(2)	−0.0202(3)	0.058(2)
C(3)	0.3419(2)	0.2067(1)	0.0402(2)	0.035(2)
C(31)	0.2365(2)	0.2311(1)	−0.0060(3)	0.044(2)
C(32)	0.1493(2)	0.1954(1)	0.0027(3)	0.045(2)
C(33)	0.0984(3)	0.1636(2)	−0.0869(3)	0.060(2)
C(34)	0.0207(3)	0.1302(2)	−0.0782(4)	0.077(3)
C(35)	−0.0068(3)	0.1277(2)	0.0211(4)	0.084(3)
C(36)	0.0402(3)	0.1603(2)	0.1090(4)	0.086(3)
C(37)	0.1173(3)	0.1942(2)	0.0997(3)	0.069(3)
C(4)	0.4058(2)	0.2107(1)	0.1532(3)	0.037(2)
C(41)	0.3803(3)	0.2366(1)	0.2522(3)	0.045(2)
C(42)	0.3651(3)	0.1978(1)	0.3398(3)	0.046(2)
C(43)	0.3114(3)	0.1506(2)	0.3116(3)	0.062(2)
C(44)	0.2940(4)	0.1171(2)	0.3947(5)	0.089(4)
C(45)	0.3293(6)	0.1308(3)	0.5048(5)	0.118(5)
C(46)	0.3834(6)	0.1783(3)	0.5344(4)	0.116(5)
C(47)	0.4024(4)	0.2110(2)	0.4531(3)	0.074(3)
C(5)	0.4962(2)	0.1818(1)	0.1601(3)	0.035(2)
C(51)	0.5812(3)	0.1731(1)	0.2661(3)	0.044(2)
C(52)	0.5828(3)	0.1184(1)	0.3204(3)	0.043(2)
C(53)	0.5101(3)	0.0795(1)	0.2801(3)	0.057(2)
C(54)	0.5164(4)	0.0306(2)	0.3361(4)	0.076(3)
C(55)	0.5948(5)	0.0208(2)	0.4317(4)	0.085(4)
C(56)	0.6670(4)	0.0593(2)	0.4718(4)	0.080(3)
C(57)	0.6617(3)	0.1077(2)	0.4175(3)	0.060(2)
C(6)	0.4265(3)	0.3181(2)	−0.1311(3)	0.055(2)
C(7)	0.5320(3)	0.3263(2)	−0.0879(3)	0.055(2)
C(8)	0.5809(3)	0.2794(2)	−0.1060(3)	0.050(2)
C(9)	0.5071(3)	0.2418(1)	−0.1561(3)	0.046(2)
C(10)	0.4100(3)	0.2659(2)	−0.1732(3)	0.048(2)
C-Hex(1)	0.0008(19)	−0.0171(4)	0.4938(45)	0.427(30)
C-Hex(2)	0.0462(12)	0.0120(6)	0.3633(17)	0.263(19)
C-Hex(3)	0.0699(17)	−0.0064(7)	0.2658(22)	0.450(28)

Compound **1** is blue both in solid state and in solution which is indicative for a monomeric structure as it is known for the $(\eta^5\text{-}C_5H_{5\text{-}n}Me_n)_2TiCl$ ($n = 3$–5) complexes [13–15]. The evidence was obtained by X-ray crystal structure analysis (vide infra) and by EPR spectroscopy for toluene and 2-methyltetrahydrofuran (MTHF) solutions of **1**. The EPR spectrum of **1** in toluene solution has all features of the monomeric titanocene monochlorides. A broad single line $\Delta H = 1.0$ mT at $g = 1.9570$ at room temperature and strongly

TABLE 4. Atomic parameters of **3**

Atom	x	y	z	U_{eq}
Ti(1)	0.39213(6)	0.28136(6)	0.15975(5)	0.042(1)
C(1)	0.5858(3)	0.2715(3)	0.1731(3)	0.043(2)
C(11)	0.6295(4)	0.2141(4)	0.1056(3)	0.054(3)
C(12)	0.5753(4)	0.2036(4)	0.0103(3)	0.055(3)
C(13)	0.4624(5)	0.1228(4)	−0.0237(3)	0.069(3)
C(14)	0.4114(6)	0.1089(5)	−0.1124(4)	0.088(4)
C(15)	0.4776(8)	0.1777(7)	−0.1651(4)	0.096(5)
C(16)	0.5886(7)	0.2560(6)	−0.1316(4)	0.092(5)
C(17)	0.6395(5)	0.2708(4)	−0.0437(3)	0.071(3)
C(2)	0.5331(3)	0.2205(3)	0.2407(3)	0.045(2)
C(21)	0.5002(4)	0.0989(4)	0.2557(3)	0.059(3)
C(22)	0.5946(4)	0.0781(4)	0.3173(3)	0.054(3)
C(23)	0.5622(5)	0.0134(4)	0.3825(3)	0.069(3)
C(24)	0.6476(6)	−0.0093(5)	0.4386(4)	0.090(4)
C(25)	0.7622(6)	0.0292(5)	0.4293(4)	0.091(4)
C(26)	0.7935(5)	0.0912(6)	0.3644(4)	0.092(4)
C(27)	0.7112(4)	0.1169(5)	0.3091(3)	0.075(4)
C(3)	0.5229(3)	0.3058(4)	0.2963(3)	0.047(2)
C(31)	0.4806(4)	0.2902(5)	0.3800(3)	0.066(3)
C(32)	0.5713(5)	0.3001(4)	0.4601(3)	0.064(3)
C(33)	0.5341(6)	0.2935(5)	0.5381(3)	0.094(4)
C(34)	0.6111(10)	0.2928(7)	0.6120(5)	0.147(6)
C(35)	0.7223(10)	0.3029(7)	0.6098(6)	0.145(7)
C(36)	0.7623(7)	0.3137(5)	0.5339(5)	0.114(5)
C(37)	0.6859(5)	0.3121(5)	0.4576(4)	0.083(4)
C(4)	0.5677(3)	0.4092(3)	0.2616(3)	0.045(2)
C(41)	0.5760(4)	0.5227(4)	0.3009(3)	0.068(3)
C(42)	0.7018(4)	0.6113(4)	0.3331(3)	0.062(3)
C(43)	0.7768(5)	0.5948(5)	0.3999(4)	0.083(4)
C(44)	0.8935(6)	0.6743(8)	0.4288(5)	0.115(5)
C(45)	0.9336(8)	0.7683(8)	0.3918(6)	0.131(6)
C(46)	0.8629(10)	0.7875(7)	0.3257(6)	0.149(7)
C(47)	0.7440(7)	0.7079(5)	0.2964(5)	0.119(5)
C(5)	0.6086(3)	0.3880(3)	0.1861(3)	0.044(2)
C(51)	0.6784(4)	0.4756(4)	0.1355(3)	0.050(2)
C(52)	0.8108(4)	0.5003(3)	0.1521(3)	0.048(2)
C(53)	0.8672(4)	0.4765(4)	0.2264(3)	0.061(3)
C(54)	0.9879(5)	0.5024(5)	0.2393(4)	0.081(4)
C(55)	1.0521(5)	0.5508(5)	0.1777(5)	0.086(4)
C(56)	0.9962(5)	0.5736(5)	0.1054(4)	0.086(4)
C(57)	0.8756(4)	0.5499(4)	0.0916(3)	0.065(3)
C(61)	0.3960(4)	0.4348(4)	0.0873(3)	0.059(3)
C(62)	0.3921(4)	0.3488(4)	0.0251(3)	0.058(3)
C(63)	0.2796(4)	0.2582(4)	0.0134(3)	0.061(3)
C(64)	0.2146(4)	0.2890(4)	0.0666(3)	0.065(3)
C(65)	0.2863(4)	0.3967(4)	0.1137(3)	0.063(3)
C(7)	0.2641(4)	0.1263(4)	0.1809(3)	0.050(3)
Si(7)	0.17071(12)	−0.02749(11)	0.14914(10)	0.062(1)
C(71)	0.1982(5)	−0.1097(4)	0.2375(4)	0.095(4)
C(72)	0.0098(4)	−0.0522(5)	0.1322(4)	0.090(4)
C(73)	0.1966(6)	−0.0831(5)	0.0454(4)	0.096(4)
C(8)	0.2613(4)	0.2084(4)	0.2316(3)	0.049(2)
Si(8)	0.16770(13)	0.23842(13)	0.30183(10)	0.066(1)
C(81)	0.0259(5)	0.2268(5)	0.2306(4)	0.092(4)
C(82)	0.1350(5)	0.1343(5)	0.3818(4)	0.085(4)
C(83)	0.2396(5)	0.3861(5)	0.3618(4)	0.093(4)

TABLE 5. Selected bond distances (Å) and valence angles (°) for **1**

Ti(1)-Cl(1)	2.363(1)				
Ti(1)-C(1)	2.369(4)	Ti(1)-C(2)	2.379(4)	Ti(1)-C(3)	2.373(4)
Ti(1)-C(4)	2.381(4)	Ti(1)-C(5)	2.357(4)	Ti(1)-CE(1)	2.042(4)
C(1)-C(2)	1.412(5)	C(1)-C(11)	1.516(6)	C(11)-C(12)	1.521(6)
C(2)-C(3)	1.421(6)	C(2)-C(21)	1.514(6)	C(21)-C(22)	1.510(6)
C(3)-C(4)	1.421(6)	C(3)-C(31)	1.505(6)	C(31)-C(32)	1.507(7)
C(4)-C(5)	1.413(6)	C(4)-C(41)	1.502(6)	C(41)-C(42)	1.511(6)
C(5)-C(1)	1.417(6)	C(5)-C(51)	1.518(6)	C(51)-C(52)	1.513(6)
Ti(1)-C(6)	2.344(5)	Ti(1)-C(7)	2.344(5)	Ti(1)-C(8)	2.371(5)
Ti(1)-C(9)	2.364(5)	Ti(1)-C(10)	2.364(5)	Ti(1)-CE(2)	2.034(4)
C(6)-C(7)	1.401(7)	C(7)-C(8)	1.412(7)	C(8)-C(9)	1.395(7)
C(9)-C(10)	1.396(7)	C(10)-C(6)	1.403(7)		
CE(1)-Ti(1)-CE(2)	138.0(2)				
C(1)-C(11)-C(12)	112.9(4)	C(2)-C(21)-C(22)	116.6(3)		
C(3)-C(31)-C(32)	117.4(4)	C(4)-C(41)-C(42)	111.9(4)		
C(5)-C(51)-C(52)	117.5(4)				

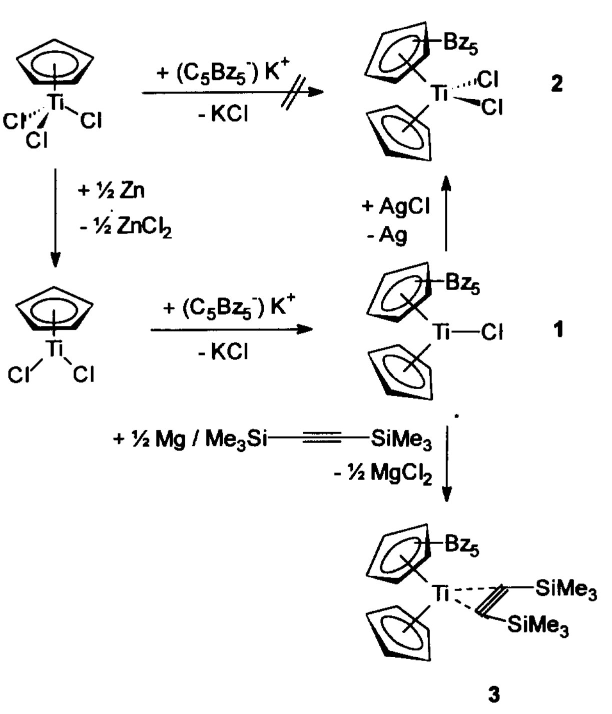
CE(1) Centre of the atoms C(1), C(2), C(3), C(4), C(5)
CE(2) Centre of the atoms C(6), C(7), C(8), C(9), C(10)

anisotropic spectrum in frozen glass (Fig. 1A) closely resemble the EPR spectra of monomeric $(\eta^5\text{-}C_5H_2Me_3)_2TiCl$, $(\eta^5\text{-}C_5HMe_4)_2TiCl$ or $(\eta^5\text{-}C_5Me_5)_2TiCl$ [15]. Two slightly different values of the g-tensor components g'_3 and g''_3 can be accounted by the presence of two conformers at low temperature, differing probably by the orientation of the Bz groups. In MTHF solution, two signals were observed at room temperature. The minor signal at $g = 1.9793$, $\Delta H = 0.5$ mT, and $a(Ti_{7/2,\ 5/2}) = 1.17$ mT was attributable to $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Bz_5)TiCl \cdot MTHF$ and the major was virtually identical with that of the non coordinated **1** observed in the toluene solution. The minor signal increased in intensity with decreasing temperature on the account of decreasing intensity of the latter one. The spectrum of non coordinated **1** practically disappeared below −70°C. In frozen MTHF glass at −140°C, the spectrum of $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Bz_5)TiCl \cdot MTHF$ with moderately anisotropic orthorhombic g-tensor (Fig. 1B) and the $g_{average}$ value close to g_{iso} was obtained. Its EPR parameters are similar to those of $(\eta^5\text{-}C_5H_5)_2TiCl \cdot MTHF$ [16] and $(\eta^5\text{-}C_5H_2Me_3)_2TiCl \cdot MTHF$ [15]. The coordination of MTHF to **1** at low temperature was also demonstrated by the colour change from blue to pale turquois. The electronic absorption spectrum taken at −20°C showed a new, very broad band of low intensity at 700–1100 nm, similar to that of $(\eta^5\text{-}C_5H_5)_2TiCl \cdot MTHF$ [17]. The reactivity of **1** with respect to MTHF can be compared with that of $(\eta^5\text{-}C_5H_2Me_3)_2TiCl$ which also yielded a mixture of the non-coordinated and coordinated complexes at ambient temperature and the coordinated

TABLE 6. Selected bond distances (Å) and valence angles (°) for **2**

Ti(1)-Cl(1)	2.348(1)	Ti(1)-Cl(2)	2.358(1)		
Ti(1)-C(1)	2.457(3)	Ti(1)-C(2)	2.434(3)	Ti(1)-C(3)	2.384(3)
Ti(1)-C(4)	2.451(3)	Ti(1)-C(5)	2.497(3)	Ti(1)-CE(1)	2.126(3)
C(1)-C(2)	1.421(4)	C(1)-C(11)	1.518(5)	C(11)-C(12)	1.521(5)
C(2)-C(3)	1.421(4)	C(2)-C(21)	1.514(4)	C(21)-C(22)	1.522(5)
C(3)-C(4)	1.429(4)	C(3)-C(31)	1.519(5)	C(31)-C(32)	1.515(5)
C(4)-C(5)	1.412(4)	C(4)-C(41)	1.506(5)	C(41)-C(42)	1.510(5)
C(5)-C(1)	1.418(4)	C(5)-C(51)	1.503(5)	C(51)-C(52)	1.521(5)
Ti(1)-C(6)	2.410(4)	Ti(1)-C(7)	2.409(4)	Ti(1)-C(8)	2.403(4)
Ti(1)-C(9)	2.365(4)	Ti(1)-C(10)	2.385(4)	Ti(1)-CE(2)	2.076(5)
C(6)-C(7)	1.404(6)	C(7)-C(8)	1.396(5)	C(8)-C(9)	1.392(5)
C(9)-C(10)	1.417(5)	C(10)-C(6)	1.401(5)		
Cl(1)-Ti(1)-Cl(2)	93.8(0)	CE(1)-Ti(1)-CE(2)	133.6(2)		
C(1)-C(11)-C(12)	119.3(3)	C(2)-C(21)-C(22)	112.0(3)		
C(3)-C(31)-C(32)	114.6(3)	C(4)-C(41)-C(42)	114.4(3)		
C(5)-C(51)-C(52)	115.4(3)				

CE(1) Centre of the atoms C(1), C(2), C(3), C(4), C(5)
CE(2) Centre of the atoms C(6), C(7), C(8), C(9), C(10)



Scheme 1.

complex in the frozen MTHF glass [15]. However, g_{iso} and g_{av} of **1** in toluene solution and glass are practically the same as those of $(\eta^5\text{-}C_5Me_5)_2TiCl$ [15]. This is surprising in view of decreasing g_{iso} in the series of the complexes $(\eta^5\text{-}C_5H_{5\text{-}n}Me_n)TiAl_2Cl_{8\text{-}x}Et_x$ ($n = 0$–5; $x = 0$–4) with increasing n values (for the same x) [18] whereas the acidity of the parent hydrocarbons is decreasing in the order $C_5H_6 > C_5Bz_5H > C_5Me_5H$ [19].

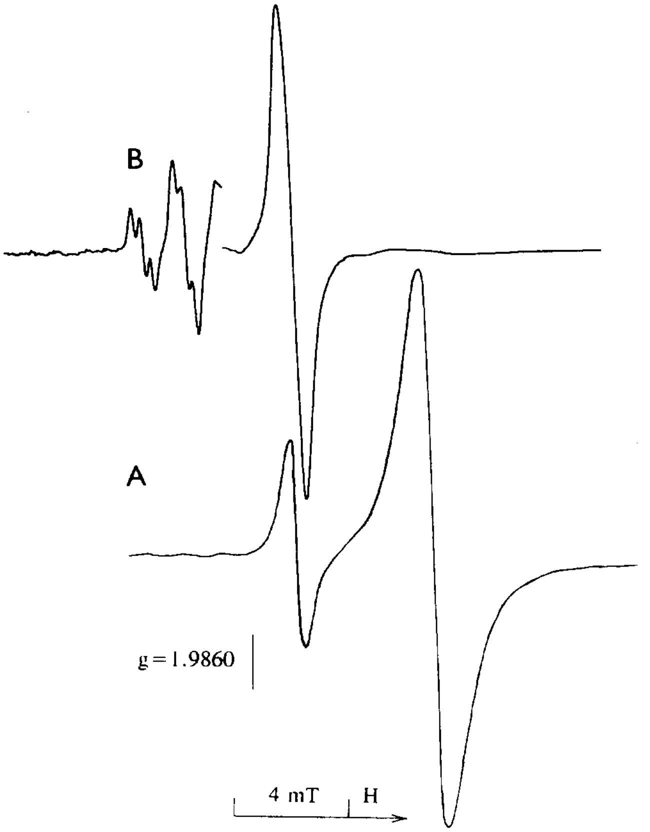


Fig. 1. EPR spectra of **1** in toluene (A) and in MTHF (B) both at −140°C.

The reason can be sought in the high polarisability of the phenyl rings in the C_5Bz_5 ligand [20] which enables the delocalisation of the unpaired electron over the

TABLE 7. Selected bond distances (Å) and valence angles (°) for **3**

Ti(1)–C(7)	2.123(5)	Ti(1)–C(8)	2.102(5)		
Ti(1)–C(1)	2.40C(4)	Ti(1)–C(2)	2.408(4)	Ti(1)–C(3)	2.397(5)
Ti(1)–C(4)	2.407(4)	Ti(1)–C(5)	2.459(4)	Ti(1)–CE(1)	2.100(4)
C(1)–C(2)	1.416(6)	C(1)–C(11)	1.539(7)	C(11)–C(12)	1.518(7)
C(2)–C(3)	1.420(6)	C(2)–C(21)	1.516(7)	C(21)–C(22)	1.516(7)
C(3)–C(4)	1.427(6)	C(3)–C(31)	1.500(7)	C(31)–C(32)	1.512(8)
C(4)–C(5)	1.421(6)	C(4)–C(41)	1.514(7)	C(41)–C(42)	1.519(8)
C(5)–C(1)	1.418(6)	C(5)–C(51)	1.510(6)	C(51)–C(52)	1.527(6)
Ti(1)–C(61)	2.351(5)	Ti(1)–C(62)	2.355(5)	Ti(1)–C(63)	2.428(5)
Ti(1)–C(64)	2.486(6)	Ti(1)–C(65)	2.418(6)	Ti(1)–CE(2)	2.090(5)
C(61)–C(62)	1.413(7)	C(62)–C(63)	1.414(7)	C(63)–C(64)	1.394(8)
C(64)–C(65)	1.405(8)	C(65)–C(61)	1.409(8)		
C(7)–C(8)	1.300(7)	C(7)–Si(7)	1.861(5)	C(8)–Si(8)	1.858(5)
CE(1)–Ti(1)–CE(2)	137.3(2)	C(7)–Ti(1)–C(8)	35.8(2)		
Ti(1)–C(7)–C(8)	71.2(3)	Ti(1)–C(8)–C(7)	73.0(3)		
C(8)–C(7)–Si(7)	135.7(4)	C(7)–C(8)–Si(8)	141.0(4)		
C(1)–C(11)–C(12)	118.1(4)	C(2)–C(21)–C(22)	115.0(4)		
C(3)–C(31)–C(32)	117.1(4)	C(4)–C(41)–C(42)	114.8(4)		
C(5)–C(51)–C(52)	114.1(4)				

CE(1) Centre of the atoms C(1), C(2), C(3), C(4), C(5)
CE(2) Centre of the atoms C(61), C(62), C(63), C(64), C(65)

ligand. This effect was clearly observed in the series of $(\eta^5\text{-}C_5H_{5-n}Me_n)TiAl_2Cl_{8-x}Et_x$ and $(\eta^5\text{-}C_5Bz_5)TiAl_2Cl_{8-x}Et_x$ complexes where g_{iso} of the C_5Bz_5 complexes were by ca. 0.0010 lower than those of the C_5Me_5 complexes [6] whereas those of the C_5H_5 complexes were by ca. 0.0025 higher [18]. In **1** the opposite effects of both ligands on the value of g_{iso} are partly compensated, however, the different structure of the C_5Bz_5 ligand in **1** and in the above mentioned trinuclear complexes and some steric strain in $(\eta^5\text{-}C_5Me_5)_2TiCl$ [13] may influence their g-values in an unpredictable way.

The bright red colour of **2** is common to $(\eta^5\text{-}C_5H_{5-n}Me_n)_2TiCl_2$ compounds for $n = 0\text{–}4$ [17], $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)TiCl_2$ [21,22] and $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Ph_5)TiCl_2$ [23]. Compound **2** is, however, very sensitive to sunlight in toluene solution and rapidly decomposes to give a mauve precipitate of presumable $[(\eta^5\text{-}C_5H_5)TiCl_2]_n$. The yellow diamagnetic compound **3** is comparable with $(\eta^5\text{-}C_5Me_5)_2Ti[\eta^2\text{-}(CSiMe_3)_2]$ [24] and $(C_5HMe_4)_2Ti[\eta^2\text{-}(CSiMe_3)_2]$ [25] which all yield very similar electronic absorption spectra dominated by an absorption band at 920 nm and similar NMR spectra for the BTMSA ligand.

3.2. *Crystal structures of 1, 2, and 3*

The results of the X-ray crystal structure analyses of **1**, **2**, and **3** revealed that the compounds have structures very similar to known symmetrical and asymmetrical titanocene derivatives. The asymmetry introduced by one bulky C_5Bz_5 ligand into the titanocene moiety will be described by the difference in the angles CE–Ti–CE (CE(1) = centroid of the C_5Bz_5 ring, CE(2) = centroid of the C_5H_5 ring and CE(3) = centroid of the additional atoms of the ligand, which are bonded to the Ti atom) and ϕ_1 and ϕ_2, respectively (see Fig. 2). Important common structural features of **1**, **2**, and **3** are listed in Table 8.

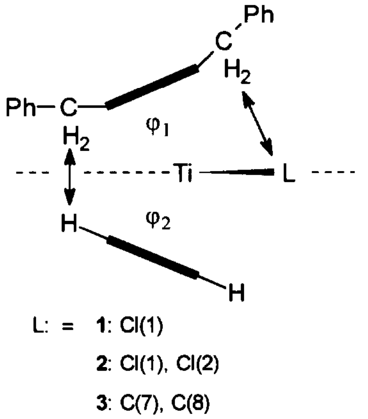


Fig. 2. Diagram of the angles ϕ_1 and ϕ_2 for **1**, **2** and **3**; sterical repulsions (see text) are depicted by bold arrows.

Compound **1** is monomeric with a planar-triangular coordination around the titanium atom. The C_5Bz_5 and C_5H_5 ring are in staggered conformation with one carbon atom of the C_5H_5 ring pointing to the edge of the wedge formed by the planes of the C_5H_5 and C_5Bz_5 rings (Fig. 3). The Ti–CE(1) distance (2.042(4) Å falls between the values for $(\eta^5\text{-}C_5Me_5)_2TiCl$ (2.06(2)

TABLE 8. Comparison of the $(\eta^5\text{-}C_5H_5)$ $(\eta^5\text{-}C_5Bz_5)$ Ti-moities in the complexes **1**, **2** and **3** (bond distances (Å), angles (°), for definition of ϕ_1 and ϕ_2 see Fig. 2, ϕ_3 is the angle between the least squares planes of the C_5Bz_5 ring and C_5H_5 ring [a]

	1	**2**	**3**
Ti–C(Cp^{Bz})	2.372(9)	2.445(37)	2.422(23)
Ti–C(Cp)	2.357(11)	2.394(17)	2.408(50)
Ti–CE(1)	2.042(4)	2.126(3)	2.100(4)
Ti–CE(2)	2.034(4)	2.076(5)	2.090(5)
C(Cp^{Bz})–C(Cp^{Bz})	1.417(4)	1.420(5)	1.420(6)
C(Cp^{Bz})–C	1.511(6)	1.512(6)	1.516(13)
C–C(Ph)	1.512(5)	1.518(5)	1.518(8)
C(Cp)–C(Cp)	1.401(8)	1.402(9)	1.407(8)
Ti–Cl	2.363(1)	2.353(5)	–
Ti–C(BTMSA)	–	–	2.113(11)
C(Cp^{Bz})–C–C(Ph), up	113.8(20)	114.1(13)	115.3(11)
C(Cp^{Bz})–C–C(Ph), down	117.5(4)	119.3(3)	118.1(4)
CE(1)–Ti(1)–CE(2)	138.0(2)	133.6(2)	137.3(2)
CE(1)–Ti(1)–CE(3)	111.4(1)	115.2(1)	113.6(2)
CE(2)–Ti(1)–CE(3)	110.4(1)	112.2(1)	108.5(2)
ϕ_1	21.6	26.8	22.1
ϕ_2	21.1	22.5	23.3
ϕ_3	42.8	49.2	45.3
CE(3) Centre of	Cl(1)	Cl(1), Cl(2)	C(7), C(8)

[a] The angle between the normals to the C_5-rings is equal to $180° - \phi_3$.

Å) [13] and (η^5-$C_5HMe_4)_2TiCl$ (2.031 Å) [14] while the Ti–CE(2) (2.034(4) Å) distance is slightly shorter than that in [(η^5-$C_5H_5)_2TiCl]_2$ (av. 2.054 Å) [26]. The CE(1)–Ti–CE(2) angle (138.0(2)°) in **1** is smaller than that of (η^5-$C_5Me_5)_2TiCl$ (143.6(2)°) and of $(C_5HMe_4)_2TiCl$ (139.1°), indicating only a low steric hindrance between the C_5H_5 and C_5Bz_5 ligands. Nearly equal angles CE(1)–Ti–Cl (111.4(1)°) and CE(2)–Ti–Cl (110.4(1)°) as well as ϕ_1 (21.6°) and ϕ_2 (21.1°), respectively, indicate a negligible steric effect of the C_5Bz_5 ligand. All methylene carbon atoms of the benzyl substituents are declined from the least square plane of the C(1)–C(5) ring away from the titanium atom. Among them, C(41) shows the largest displacement out of the C_5–plane (0.25 Å), probably as a result of some repulsion of the methylene group with the chlorine atom (nonbonding distance C(41)–Cl(1) 3.250(4) Å). The Ti(1)–Cl(1) bond length of 2.363(1) Å is virtually the same as in (η^5-$C_5Me_5)_2TiCl$, both being longer than that in (η^5-$C_5HMe_4)_2TiCl$ (2.317 Å). The arrangement of the benzyl substituents of the C_5Bz_5 ligand will be discussed below for all the compounds **1–3**.

The molecular structure of **2** (Fig. 4) resembles structures of other titanocene dichlorides, the structures of asymmetrical (η^5-C_5H_5)(η^5-$C_5Me_5)TiCl_2$ [21,22], (η^5-C_5H_5)(η^5-$C_5Ph_5)TiCl_2$ [23] and (η^5-C_5H_5)(η^5-C_5H_2(1,2,4-$(SiMe_3)_3)TiCl_2$ [27] being most relevant. The C_5H_5 and C_5Bz_5 ligands in **2** are staggered, however, in contrast to **1**, with one carbon atom of the C_5Bz_5 ring pointing to the edge of the wedge. The CE(1)–Ti–CE(2) angle of **2** (133.6(2)°) falls between that of $(C_5H_5)(C_5Me_5)TiCl_2$ (132°) and that of $(C_5H_5)(C_5Ph_5)TiCl_2$ (134.9°). The Ti–CE(1) (2.126(3) Å) and Ti–CE(2) (2.076(5) Å) distances are very close to the relevant distances in (η^5-C_5H_5)(η^5-$C_5Me_5)TiCl_2$ (2.10 and 2.06 Å). The Ti–Cl bond distance in **2** (av. 2.353(3) Å) is virtually the same as in (η^5-$C_5Me_5)_2TiCl_2$ (av. 2.351(2) Å) [28] and (η^5-C_5H_5)(η^5-$C_5Me_5)TiCl_2$ (av. 2.349 (1) Å) [21,22], but slightly shorter than in (η^5-$C_5H_5)_2TiCl_2$ (av. 2.364(3) Å) [29]. The value of the Cl–Ti–Cl angle (93.8(0)°) lies between those for (η^5-$C_5HMe_4)_2TiCl_2$ (94.2°) [14] and (η^5-$C_5Me_5)_2TiCl_2$ (92.9°) [28]. The staggered configuration in **2** implies a strong repulsive interaction between the chlorine atoms and the hydrogen atoms of the methylene groups of the C_5Bz_5 ligand. The nonbonding distances Cl(1)–C(51) (3.115(3) Å and Cl(2)–C(41) (3.074(4) Å) are responsible for the asymmetry of the (η^5-C_5H_5)(η^5-C_5Bz_5)Ti(CE(3)) skeleton which is reflected in a large difference between ϕ_1 (26.8°) and ϕ_2 (22.5°). Similar Cl--(H) repulsions were found for the asymmetrical complexes (η^5-C_5H_5)(η^5-$C_5Ph_5)TiCl_2$ ($\phi_1 = 27.5°$, $\phi_2 = 21.6°$) [23] or (η^5-C_5H_5)(η^5-1,2,4-$(SiMe_3)_3C_5H_2)TiCl_2$ ($\phi_1 = 27.0°$, $\phi_2 = 23.4°$) [27]. The correlation between the mode of staggering and the presence of the above mentioned steric hindrance seems to be confirmed by the crystal structure of (η^5-C_5H_5)(η^5-$C_5Me_5)TiCl_2$ where one carbon atom of the C_5H_5 ring is pointing to the edge of the wedge of the cyclopentadienyl ring planes [21,22]. The absence of sterical hindrance in (η^5-C_5H_5)(η^5-$C_5Me_5)TiCl_2$ follows from the nearly equal values of ϕ_1 (26.5°), and ϕ_2 (25.6°) angles whereas the CE(1)–Ti–CE(2) angle is close to that of **2**. The methylene carbon atoms of **2** are mostly pointing away from the least square plane formed by the

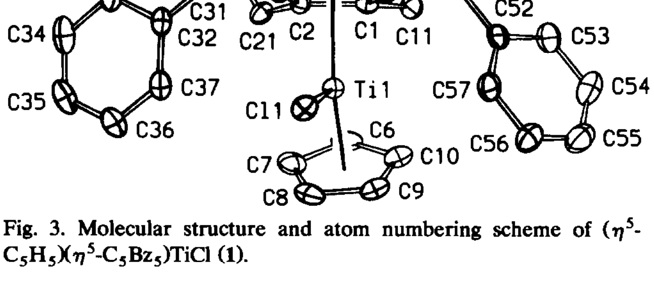


Fig. 3. Molecular structure and atom numbering scheme of (η^5-C_5H_5)(η^5-C_5Bz_5)TiCl (**1**).

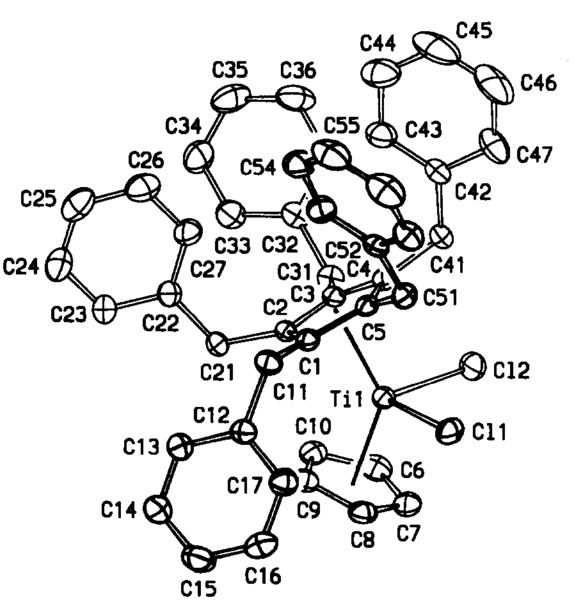


Fig. 4. Molecular structure and atom numbering scheme of (η^5-C_5H_5)(η^5-$C_5Bz_5)TiCl_2$ (**2**).

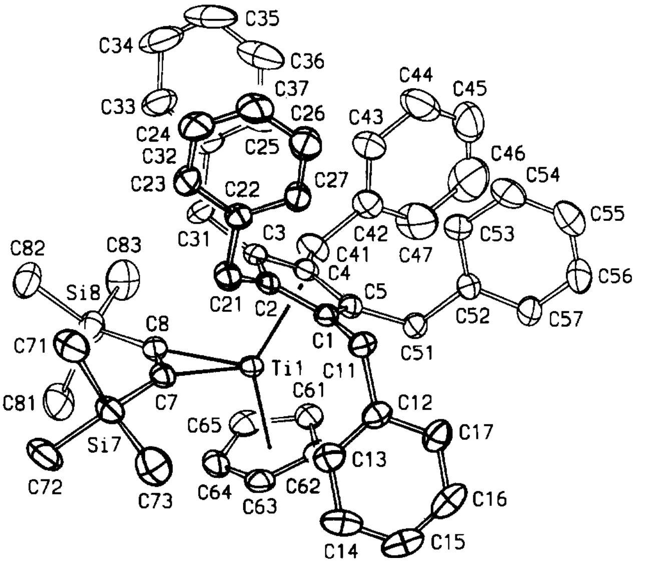


Fig. 5. Molecular structure and atom numbering scheme of $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Bz_5)Ti[\eta^2\text{-}(CSiMe_3)_2]$ (3).

C(1)–C(5) atoms (Table 8). Among them, C(21), which is located close to the edge of the wedge, shows the highest deviation from this plane (0.37 Å). This apparently results from the repulsive interaction between the C_5H_5 and C_5Bz_5 ligands and between the methylene groups and Cl atoms which is indicated by the large value of ϕ_1 compared with ϕ_2.

The Ti(II)–acetylene complex 3 contains the cyclopentadienyl rings in a staggered conformation analogous to that in 2 (Fig. 5). The Ti–CE(1) and Ti–CE(2) distances are very close to those of 2 (Table 8). However, the steric repulsion between the BTMSA and C_5Bz_5 ligands is very low as follows from a large CE(1)–Ti–CE(2) angle (137.3(2)°) and from small and nearly equal angles ϕ_1 (22.1°) and ϕ_2 (23.3°). The Ti–C(ac) (av. 2.42(2) Å) and C(ac)–C(ac) distances and the C(ac)–C(ac)–Si angle (av. 138(3)°) (the silicon atom declined farther away from titanium) are only slightly different from those found in $(\eta^5\text{-}C_5HMe_4)_2Ti[\eta^2\text{-}C_2(SiMe_3)_2]$ (2.106(3) Å, 1.303(5) Å, 140(2)°) [25] and $(\eta^5\text{-}C_5Me_5)_2Ti[\eta^2\text{-}C_2(SiMe_3)_2]$ (2.124(3) Å, 1.309(4) Å, 135.9(5)°) [24]. Bending of the BTMSA ligand upon coordination to a transition metal is a commonly observed phenomenon which is brought about by the change of hybridisation of the acetylenic carbon atoms from sp to sp^2 [30]. The asymmetry of the $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Bz_5)Ti$ moiety in 3 induces some asymmetry in the coordination of the $(\eta^2\text{-}C_2(SiMe_3)_2$ ligand. The silicon atoms are declined by 0.225 Å (Si(7)) and 0.285 Å (Si(8)) from the Ti(1), C(7), C(8) plane towards the C_5H_5 ring. This corresponds to an angle of 11.8° between the Ti(1), C(7), C(8) plane and the least square plane of Si(7), C(7), C(8), Si(8). The absence of the steric hindrance in 3 is also indicated by the lowest maximum deviation of the methylene carbon atoms from the least square plane of the C_5Bz_5 ring amongst the studied compounds (Table 8).

The arrangement of the benzyl substituents differs in 1, 2 and 3 from the only known titanium derivative $(\eta^5\text{-}C_5Bz_5)Ti(AlCl_4)_2$ where all the benzyl groups are orientated away from the titanium atom (up-orientation) [6]. In 1 two benzyl groups are orientated towards the titanium atom (down-orientation) (Fig. 3) whereas in both 2 and 3 only one benzyl group (attached to C(1)) is orientated in this way (Figs. 4 and 5). The structure of the benzyl groups differ for their up and down orientations: the C(Cp)–CH_2–C(Ph) angle is always significantly larger for the down orientation (see Table 8). The same phenomenon has been observed for all so far known C_5Bz_5 complexes [1–6]. In the case of $(C_5Bz_5)_2Sn$ an interaction between the aromatic ring of the Bz substituent and a lone electron pair of the metal atom was assumed on the base of SCF–Xα–SW calculations [31]. Analogous interactions can be sought in 1, 2, and 3 using the MO model for bent Cp_2M fragments by Lauher and Hoffmann [32]. Of the three lowest energy frontier orbitals $1a_1$, b_2 and $2a_1$ only $1a_1$ extends efficiently to the region where aromatic rings of the bent-down Bz groups are located. The largest overlap of $1a_1$ with aromatic ring orbitals of the same symmetry can occur in 1 where two aromatic rings are available. The close contacts between the titanium atom and the phenyl groups C(32)–C(37) and C(52)–C(57) were found for the ortho carbon atoms Ti–C(37) 3.671(5) Å and Ti–C(57) 3.557(5) Å. The angle C(37)–Ti–C(57) 157.7(1)° is large enough to place the carbon atoms into the overlap area of the $1a_1$ orbital. In the compounds 2 and 3 an analogous interaction of the $1a_1$ orbital with one bent-down benzyl group is possible (cf. Figs. 4 and 5). However, the relevance of the interaction for the molecular structure in the solid state is difficult to evaluate. Tentatively, it seems that the arrangements with some down-orientated Bz groups is energetically favourable. From the point of view of the steric hindrance between the C_5Bz_5-ring and the two chlorine atoms (2) and the BTMSA ligand (3), respectively, the disadvantageous staggering of the C_5-rings in 2 and 3 is overweighted by the interaction of the aromatic ring with the Ti atom. In 1 the interaction of the orbital $1a_1$, containing the unpaired electron, with two bent-down phenyl group, of the C_5Bz_5 substituents can account for the low g-value (g_{iso} = 1.957 and the g-tensor values with average of g'_3 and g''_3 are the same as those for $(\eta^5\text{-}C_5Me_5)_2TiCl$ [15]). It is possible that the interaction through down-orientated aromatic rings will further decrease the unpaired electron density on the C_5Bz_5 ligand which will result in the larger negative contribution to the *g*-value to compensate the positive contribution from the C_5H_5 ligand.

The effect of the titanium valency is difficult to subtract from other effects influencing the structure of the investigated $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Bz_5)$Ti compounds.

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