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Preparation and crystal structure of (η^5-pentabenzylcyclopentadienyl)- and (η^5-cyclopentadienyl)-titanium(III) bis(tetrachloroaluminate) complexes

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Abstract

The complexes (η^5-C_5Bz_5)Ti($AlCl_4$)$_2$ (Bz = benzyl) (**I**) and (η^5-C_5H_5)Ti($AlCl_4$)$_2$ (**II**) were obtained by the redox reaction of (η^6-C_6H_6)Ti($AlCl_4$)$_2$ (**III**) with the corresponding cyclopentadienes. Single crystal X-ray analysis revealed that **I** is triclinic (space group $P\bar{1}$, *a* 10.449(2), *b* 13.530(2), *c* 17.074(3) Å, α 95.62(2), β 103.89(2), γ 112.70(2)°) and **II** is monoclinic ($P2_1/n$, *a* 13.710(4), *b* 13.139(5), *c* 9.666(2) Å, β 106.90(2)°). The molecular structures of **I** and **II** differ in common features only negligibly from that of **III**. The C_5Bz_5 ligand in **I** exhibits a crown structure with Bz groups orientated uniformly away from the titanium atom. Compound **II** has a remarkably short Ti–(η^5-C_5H_5) ring distance (1.98 Å). Introduction of ethyl (Et) groups into outer positions of aluminate ligands in **I** induced changes in ESR and UV-Vis spectra similar to those known for derivatives of **II** and analogous η^5-C_5Me_5 complexes.

1. Introduction

The (η^5-C_5H_5)Ti($AlCl_4$)$_2$ complex (**II**) was first reported to arise from the reduction of (η^5-C_5H_5)$TiCl_3$ with aluminium in the presence of $AlCl_3$ (eqn. (1)) or from the protolysis of (η^5-C_5H_5)$_2$Ti($AlCl_4$) in the presence of $AlCl_3$ (eqn. (2)) [1]. Its trinuclear Al-Ti-Al structure was deduced from its ESR eleven-line spectrum which indicated the interaction of Ti^{III} d^1 electron with two equivalent Al nuclei ($I_N = 5/2$). Subsequently, compound **II** was also prepared by the redox reaction of one equivalent of cyclopentadiene (C_5H_6) with (η^6-C_6H_6)Ti^{II}($AlCl_4$)$_2$ (**III**) according to eqn. (3) [2,3]

$$3(\eta^5\text{-}C_5H_5)TiCl_3 + Al + n\,AlCl_3 \rightarrow 3\mathbf{II} + (n-5)AlCl_3 \qquad (1)$$

$$(\eta^5\text{-}C_5H_5)_2Ti(AlCl_4) + AlCl_3 + HCl \rightarrow \mathbf{II} + C_5H_6 \qquad (2)$$

$$\mathbf{III} + C_5H_6 \rightarrow \mathbf{II} + C_6H_6 + H\cdot \qquad (3)$$

Reactions analogous to eqn. (3) proceeded also with methyl-substituted cyclopentadienes, including the weakest acid pentamethylcyclopentadiene (C_5Me_5H) [4].

Although the trinuclear structure of **II** and other (η^5-$C_5H_{5-z}Me_z$)Ti^{III}($AlCl_4$)$_2$ (z = 0–5) compounds

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were established without doubt [1–4], no X-ray crystallographic data are available for any compound of the series. On the other hand, crystal and molecular structures of (arene)titanium(II) complexes (**III** and its derivatives) are well known and their trinuclear Al–Ti–Al inorganic skeleton was found to be practically unaffected by the nature of arene ligand [5–7] and by the presence of Et substituents in aluminate ligands [8]. Hence, we proposed to carry out X-ray crystallographic investigation of single crystals of **II**, parent compound of the series, and $(\eta^5\text{-}C_5Me_5)Ti(AlCl_4)_2$ (**IV**); amongst them the largest difference in oxidation potentials is to be expected [9]. Both complexes were readily prepared in solution according to eqn. (3) [4], however, the latter compound appeared to be labile in the solid state. Since we had also become interested in the effects of bulky ligands, *e.g.*, pentaphenylcyclopentadienide [10] and pentabenzylcyclopentadienide $(C_5Bz_5^-)$ anions, on the stability and reactivity of organotitanium complexes, we attempted the preparation of $(\eta^5\text{-}C_5Bz_5)Ti(AlCl_4)_2$ (**I**) where the lower electron donation ability of Bz groups compared to Me groups in **IV** can result in higher stability of **I**.

Pentabenzylcyclopentadiene (C_5Bz_5H) as a starting material was first prepared only in 1978 [11] and the first transition metal C_5Bz_5 complexes, $(\eta^5\text{-}C_5Bz_5)Co(CO)_2$ and $(\eta^5\text{-}C_5Bz_5)Rh(CO)_2$, were described in 1986 [12]. More recently, complexes of Mn, Fe, Re, and Lu have been prepared and characterized by X-ray structural analysis [13,14].

Here we report the preparation of **I** from C_5Bz_5H and **III**, the crystal structures of **I** and **II** and the ESR and UV-Vis spectra of $(\eta^5\text{-}C_5Bz_5)TiAl_2Cl_{8-x}Et_x$ (x = 0–4) complexes formed in mixtures of **I** with triethylaluminium.

2. Experimental details

A high vacuum technique was used for preparation of complexes **I** and **II** from **III** and for the measurement of UV-Vis and ESR spectra, as described earlier [2–4]. Complex **III** was obtained and purified as described elsewhere [15]. Solvents were purified in the final step by green "dimeric titanocene" [16].

2.1. Preparation of 1,2,3,4,5-pentabenzylcyclopentadiene

The following procedure is a modification of the method by Hirsch and Bailey [11] and Chambers *et al.* [12] which affords a considerably improved yield. A three-necked one litre flask equipped with a reflux condenser and water trap, thermometer and gas inlet was flushed with argon and charged with benzyl alcohol (328 g, 3 mol; Fluka 98%, not dried). Small pieces of sodium (25 g, 1.09 mol) were added over a period of 45 min. Caution: the temperature should not be raised above 120°C, to avoid too vigorous formation of hydrogen. Tetralin (200 ml) and the solution of cyclopentadiene dimer (7 g, *ca.* 0.046 mol; Fluka 85–90%) in 50 ml of tetralin were added and the mixture was stirred under reflux for 24 h. Its boiling temperature increased from 182 to 204°C and ca. 8 ml of water was collected in the trap (the trap had been filled with tetralin before the experiment to prevent a loss of cyclopentadiene). The highly viscous reaction mixture was then cooled to room temperature and was treated with 600 ml of water. The aqueous phase was extracted three times with benzene. The combined organic phases were dried over Na_2SO_4. The solvents were removed by distillation at atmospheric pressure, and subsequently, at 22 Torr up to 100°C. The remaining yellow orange oil (*ca.* 90 ml) was dissolved in 2 l of hot methanol and the solution was cooled to −30°C and kept at this temperature overnight. The crystallization of C_5Bz_5H commenced either spontaneously or was initiated by adding seed crystals. The crude product was recrystallized by the same procedure. The yield of C_5Bz_5 (m.p. 73.5–75°C) was reproducibly 27 g (56% of theoretical).

2.2. Preparation of $(\eta^5\text{-}C_5Bz_5)Ti(AlCl_4)_2$ (I)

Colourless pentabenzylcyclopentadiene (C_5Bz_5H) 0.258 g (0.5 mmol) and *ca.* 1 mg of triphenylphosphine (PPh_3) were dissolved in 10 ml of benzene and the solution was added to 25 ml of the 0.02 M benzene solution of **III** with stirring. The blue-red colour of **III** immediately turned yellow-green. The solution was concentrated to *ca.* 5 ml and hexane (20 ml) was added. Green crystals of **I** were grown by slow evaporation of the solvent mixture in a vacuum system. The crystals were washed with the solvent, dried *in vacuo* and sealed into ampoules equipped with breakable seals. The composition of crystals was determined by X-ray crystallographic analysis (*vide infra*). The yield of **I** was 0.15 g (34% of theoretical).

2.3. Preparation of $(\eta^5\text{-}C_5H_5)Ti(AlCl_4)_2$ (II)

Monomeric cyclopentadiene (0.7 mmol) was added slowly from the gas phase to a stirred solution of **III** in benzene (3.10^{-2} M, 20 ml) according to the standard procedure [2,3]. The change **III** from blue-red to the light green colour of **II** indicated the completion of reaction (3). Warning: addition of excess C_5H_6 generates $(\eta^5\text{-}C_5H_5)_2Ti(AlCl_4)$ in a reaction in reverse to eqn. (2). The reaction solution was evaporated *in vacuo* to saturation and hexane (15 ml) was added. Light green crystals of **II** were separated from the mother liquor and were recrystallized from the same solvent mixture. The yield after recrystallization was 80 mg (22% of theory). The solutions of **II** in benzene/hexane mixture exhibited the ESR and UV-Vis characteristics listed in ref. [3].

2.4. X-ray structure determination of I and II

Crystal fragments of **I** and **II** were mounted in glass capillaries under paraffin oil. The X-ray measurements were carried out on a Phillips PW 1100 single crystal diffractometer using graphite monochromated Mo $K_\alpha$radiation (λ 0.71069 Å) at room temperature. Intensities of three check reflections for I decreased to 48% during the data collection; a time dependent intensity correction was therefore applied. The crystal of **II** did not show any decomposition. The structures were solved by direct methods for **I**, by the Patterson method for **II**, and by subsequent difference Fourier calculations. In **I** some carbon atoms of the C(51)–C(56) phenyl ring could not be satisfactorily localized. The high temperature factors of C(52) to C(56) and the evidently unreasonable location of C(54) are probably due to decomposition of the crystal rather than to thermal motion. The benzyl carbon atoms and C(3) were refined with isotropic and the remaining atoms with anisotropic temperature factors. Positional and anisotropic thermal parameters for **II** were refined by the least-squares method. Hydrogen atoms were included at their calculated positions but not refined for **II** and were completely ignored for I. The SHELX 76 [17] and MULTAN 90 [18] packages were used for the calculations. Crystallographic data for **I** and **II** and data processing details are listed in Table 1. Atom coordinates for **I** and **II** are given in Tables 2 and 3, respectively; bond lengths and angles are collected in Table 4. Atomic parameters and values of F_o and F_c have been deposited at the Cambridge Crystallographic Data Centre. Figure 1 shows a PLUTO drawing [19] of **I**.

2.5. Characterization of (η^5-C_5Bz_5)$TiAl_2Cl_{8-x}Et_x$(x = 0–4) complexes by ESR and UV-Vis spectroscopy

Benzene solutions of **III** (0.04 mmol, 2 ml) were added to a freshly prepared mixture of C_5Bz_5H with Et_3Al in benzene (0.1 M) at molar ratios C_5Bz_5H : **III** = 1 : 1 and **III** : Et_3Al = 0.5, 1.5 and 4.0. The resulting green solutions were transferred into all-sealed quartz cells (Hellma, d = 0.1 and 1.0 cm) joined to an ESR sample tube. ESR spectra were recorded on an ERS-220 spectrometer (ZWG Berlin, GDR) in X-band at room temperature. The integrated ESR spectra were compared to a standard sample containing (η^5-C_5H_5)$_2$Ti($AlCl_3$Et) (5.275×10^{-3} M) in benzene. UV-Vis absorption spectra were measured on a Varian Cary 17D spectrometer in the range 300–2000 nm. Both the measurements were analogous to those described for investigation of (η^5-C_5Me_5)$TiAl_2Cl_{8-x}Et_x$ (x = 0–4) complexes [4].

3. Results and discussion

Both compounds **I** and **II** were obtained by redox reactions of cyclopentadienes C_5Bz_5H and C_5H_6, respectively, with **III** according to eqn. (3). The isolated yields of both compounds (34 and 22%, respectively) were low because of the presence of abundant byproducts.

For obtaining **I**, the acidity of **III** was suppressed by addition of a small amount of triphenylphosphine which binds traces of free $AlCl_3$ into an inactive complex [20]; nevertheless, the yield of **I** as determined by the ESR method (*vide infra*) did not exceed 70%. Green crystals of **I** which were separated in the first crop from a concentrated solution of the reaction products were used for X-ray analysis. The solution made of these crystals gave the same ESR spectrum as that of the mother liquor, the UV-Vis spectrum was very similar to that of **IV** [4] (*vide infra*). Upon evaporation of the mother liquor, a yellow, diamagnetic byproduct formed an amorphous solid which always contained some amount of crystalline **I**. The structure of the byproduct remains unknown.

In the preparation of **II**, the monomeric cyclopentadiene is competitively consumed in a rapid polymerization reaction induced by the cationic activity of **III** and an excess C_5H_6 gives rise to (η^5-C_5H_5)$_2$Ti($AlCl_4$) [2,3]. These side reactions were partly suppressed by con-

TABLE 1. Details of the structure determination of I and **II**

	I	II
Crystal data		
Chemical formula	($C_{40}H_{35}$)$TiAl_2Cl_8$	(C_5H_5)$TiAl_2Cl_8$
Crystal System	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a, Å	10.449(2)	13.710(4)
b, Å	13.530(2)	13.139(5)
c, Å	17.074(3)	9.666(2)
Angles, deg	α 95.62(2) β 103.89(2) γ 112.70(2)	β 106.90(2)
V, Å^3	2112	1666
Z	2	4
D_{calc}, g cm^{-3}	1.417	1.80
μ, cm^{-1}	7.1	17.6
Approx. cryst. dimens., mm	0.1, 0.2, 0.6	0.2, 0.3, 0.3
Data collection and refinement		
θ_{max}, deg	18.0	27.5
Total data	3040	3285
Unique observed data		
$F_o \geq 2\sigma$ (F_o)	2182	2291
No. of refined parameters	280	145
R	0.141	0.050
R_w	0.141	0.058

ducting reaction 3 at low concentration of C_5H_6 until all **III** had been consumed.

3.1. Crystal structures of I and II

Both complexes **I** and **II** exert a square pyramidal coordination around Ti^{III} with four bridging chlorine atoms forming the pyramid base and one η^5-C_5Bz_5 or η^5-C_5H_5 ligand at its apex (see Fig. 1). The structures of **I** and **II** do not significantly differ in bond lengths and valence angles (Table 4). The Ti–(CE) (CE: centroid of C_5-ring) distances belong among the shortest (η^5-cyclopentadienyl)–Ti distances so far known [21], especially for **II**. The five-membered rings are almost perfectly planar (deviations of atoms from their least

TABLE 2. Atom coordinates and temperatures factors for (η^5-C_5Bz_5) $(AlCl_4)_2$) (**I**)

Atom	x	y	z	U[a]
Ti	0.2919(4)	0.2755(3)	0.5782(2)	0.042(2)
Al(1)	0.4091(9)	0.1753(6)	0.4273(5)	0.068(5)
Cl(11)	0.4704(6)	0.3403(4)	0.4949(3)	0.054(4)
Cl(12)	0.2427(8)	0.0981(5)	0.4877(4)	0.087(5)
Cl(13)	0.5742(9)	0.1251(6)	0.4588(5)	0.106(6)
Cl(14)	0.3197(10)	0.1635(7)	0.3033(4)	0.111(6)
Al(2)	−0.0054(8)	0.3306(8)	0.4943(5)	0.088(6)
Cl(21)	0.2298(6)	0.4230(5)	0.5230(4)	0.064(4)
Cl(22)	0.0152(7)	0.1871(6)	0.5364(4)	0.085(5)
Cl(23)	−0.0871(9)	0.4008(9)	0.5693(6)	0.130(8)
Cl(24)	−0.1071(9)	0.2929(11)	0.3695(5)	0.190(10)
C(1)	0.2726(26)	0.2432(21)	0.7111(14)	0.053(16)
C(2)	0.3753(27)	0.2105(16)	0.6944(12)	0.044(15)
C(3)	0.4928(22)	0.3007(17)	0.6847(12)	0.046(6)
C(4)	0.4580(23)	0.3925(15)	0.6938(12)	0.034(13)
C(5)	0.3256(26)	0.3591(21)	0.7103(13)	0.045(17)
C(10)	0.1327(27)	0.1708(20)	0.7250(15)	0.07(1)
C(11)	0.1595(26)	0.1399(20)	0.8118(16)	0.06(1)
C(12)	0.2425(35)	0.2129(27)	0.8857(22)	0.12(1)
C(13)	0.2197(41)	0.1454(34)	0.9582(24)	0.15(2)
C(14)	0.1373(38)	0.0359(32)	0.9323(24)	0.12(1)
C(15)	0.0838(52)	−0.0334(42)	0.8656(35)	0.20(2)
C(16)	0.0761(41)	0.0272(33)	0.7973(25)	0.15(2)
C(20)	0.3669(23)	0.0949(18)	0.6836(14)	0.06(1)
C(21)	0.4293(26)	0.0658(20)	0.7660(16)	0.07(1)
C(22)	0.4937(26)	0.1367(20)	0.8402(16)	0.07(1)
C(23)	0.5525(33)	0.1007(26)	0.9132(20)	0.11(1)
C(24)	0.5360(30)	−0.0063(25)	0.9036(19)	0.09(1)
C(25)	0.4694(36)	−0.0747(27)	0.8323(23)	0.12(1)
C(26)	0.4126(30)	−0.0480(23)	0.7593(19)	0.09(1)
C(30)	0.6304(25)	0.3040(18)	0.6664(15)	0.06(1)
C(31)	0.7243(27)	0.2798(21)	0.7395(17)	0.07(1)
C(32)	0.7880(27)	0.3469(20)	0.8174(17)	0.07(1)
C(33)	0.8760(32)	0.3264(25)	0.8802(19)	0.10(1)
C(34)	0.8885(29)	0.2252(24)	0.8715(18)	0.09(1)
C(35)	0.8242(30)	0.1537(23)	0.7976(19)	0.09(1)
C(36)	0.7359(26)	0.1806(20)	0.7268(16)	0.07(1)
C(40)	0.5587(22)	0.5112(17)	0.6886(13)	0.05(1)
C(41)	0.7012(26)	0.5689(18)	0.7604(15)	0.06(1)
C(42)	0.7018(30)	0.5879(22)	0.8401(19)	0.09(1)
C(43)	0.8334(30)	0.6455(21)	0.9067(16)	0.08(1)
C(44)	0.9559(35)	0.6823(25)	0.8860(21)	0.11(1)
C(45)	0.9607(48)	0.6639(35)	0.8039(30)	0.17(2)
C(46)	0.8216(38)	0.6000(26)	0.7363(21)	0.12(1)
C(50)	0.2435(25)	0.4257(19)	0.7230(15)	0.07(1)
C(51)	0.2776(27)	0.4804(21)	0.8110(17)	0.07(1)
C(52)	0.2451(68)	0.5413(53)	0.8388(42)	0.26(3)
C(55)	0.4080(56)	0.5264(46)	0.9773(35)	0.23(3)
C(56)	0.3733(58)	0.4650(43)	0.8849(37)	0.13(2)

[a] U_{eq} is given for atoms refined with anisotropic temperature factors and U_{iso} is given for other atoms.

TABLE 3. Atom coordinates and equivalent isotropic temperature factors for $(\eta^5\text{-}C_5H_5)\,(AlCl_4)_2$ (II)

Atom	x	y	z	U_{eq}
Ti	0.3028(1)	0.1761(1)	0.0459(1)	0.0398(4)
Al(1)	0.1137(1)	0.1858(1)	0.2047(2)	0.0605(8)
Al(2)	0.2783(1)	0.0862(1)	−0.2943(2)	0.0538(8)
Cl(11)	0.2186(1)	0.0635(1)	0.1899(2)	0.0599(8)
Cl(12)	0.1479(1)	0.2800(1)	0.0382(2)	0.0585(6)
Cl(13)	0.1655(2)	0.2669(2)	0.3975(2)	0.0860(10)
Cl(14)	−0.0345(1)	0.1310(2)	0.1471(3)	0.0927(11)
Cl(21)	0.3136(1)	0.0116(1)	−0.0822(2)	0.0591(6)
Cl(22)	0.2566(1)	0.2362(1)	−0.2143(1)	0.0555(5)
Cl(23)	0.4030(2)	0.0798(2)	−0.3753(2)	0.0636(10)
Cl(24)	0.1440(2)	0.0257(2)	−0.4278(3)	0.0678(10)
C(1)	0.4454(4)	0.2796(5)	0.0718(7)	0.072(3)
C(2)	0.3983(4)	0.3104(5)	0.1685(8)	0.071(3)
C(3)	0.4018(5)	0.2331(7)	0.2653(7)	0.079(4)
C(4)	0.4507(5)	0.1521(6)	0.2218(10)	0.082(4)
C(5)	0.4780(4)	0.1809(6)	0.1024(10)	0.081(4)

squares plane < 0.009 Å). In **I**, the methylene carbon atoms only slightly deviate from the C_5-ring plane; the maximum deviation, exhibited by C(20), is 0.09 Å (towards Ti atom). All five phenyl groups in the C_5Bz_5 ligand are directed away from the Ti atom, forming the crown conformation (see Fig. 1). This type of conformation has been found only for decabenzylferrocene [13,14]. In all other structurally characterized metal complexes with C_5Bz_5 ligands at least one phenyl group is directed towards the metal atom whereas the remaining phenyl groups are bent away [13,14,22–26]. The phenyl ring distribution can be interpreted in terms of steric and electronic factors. For compounds containing Tl, Ge, Sn, and Pb an interaction of one of the phenyl groups with the metal by a free, directed metal electron pair has been considered [24,25]. For **I** and decabenzylferrocene this type of interaction is apparently impossible because of steric hindrance.

TABLE 4. Bond distances (Å) and angles (°) in structures **I** and **II**

	I	II
Ti–Cl(11)	2.555(7)	2.528(2)
Ti–Cl(12)	2.520(8)	2.506(2)
Ti–Cl(21)	2.523(8)	2.517(2)
Ti–Cl(22)	2.544(8)	2.535(2)
Ti–C(1)	2.39(3)	2.334(7)
Ti–C(2)	2.36(2)	2.308(7)
Ti–C(3)	2.31(2)	2.286(8)
Ti–C(4)	2.25(2)	2.258(8)
Ti–C(5)	2.30(3)	2.305(8)
Ti–(CE)	1.99	1.98
Al(1)–Cl(11)	2.18(1)	2.188(2)
Al(1)–Cl(12)	2.20(1)	2.187(2)
Al(1)–Cl(13)	2.06(1)	2.084(3)
Al(1)–Cl(14)	2.06(1)	2.073(3)
Al(2)–Cl(21)	2.19(1)	2.196(2)
Al(2)–Cl(22)	2.20(1)	2.169(2)
Al(2)–Cl(23)	2.05(1)	2.079(3)
Al(2)–Cl(24)	2.05(2)	2.075(3)
C–C (C_5-ring)	1.41 ± 0.02	1.37 ± 0.02
C–C (C_5–CH_2–)	1.52 ± 0.03	–
C–C (–CH_2–Ph)	1.54 ± 0.02	–
Cl(11)–Ti–Cl(12)	77.9(2)	79.4(1)
Cl(11)–Ti–Cl(21)	79.0(2)	82.5(1)
Cl(11)–Ti–Cl(22)	132.1(3)	134.9(1)
Cl(12)–Ti–Cl(21)	123.2(3)	128.6(1)
Cl(12)–Ti–Cl(22)	80.7(3)	80.5(1)
Cl(21)–Ti–Cl(22)	77.8(2)	79.2(1)
Cl(11)–Al(1)–Cl(12)	93.4(4)	94.7(1)
Cl(13)–Al(1)–Cl(14)	116.8(5)	118.1(1)
Cl(21)–Al(2)–Cl(22)	93.0(4)	95.1(1)
Cl(23)–Al(2)–Cl(24)	117.4(6)	115.4(1)
C–C–C(Cp–CH_2–Ph)	113(2)	–

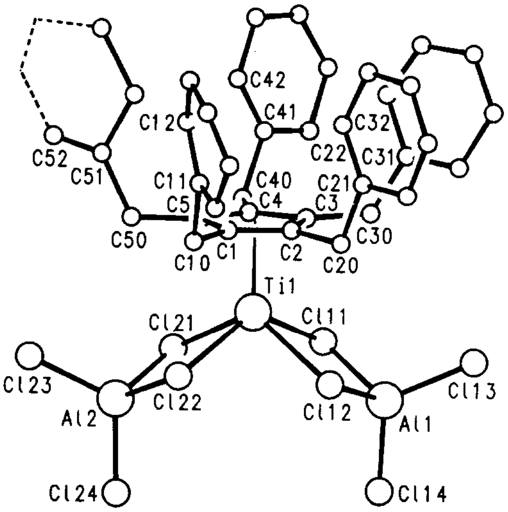

Fig. 1. Molecular structure of $(\eta^5\text{-}C_5Bz_5)Ti(AlCl_4)_2$ (**I**) drawn with the PLUTO pragram [19]. Atoms of the dashed part of the C(51) phenyl group could not be localized with certainty.

TABLE 5. Comparison of X-ray structure parameters for **I**, **II**, **III** [5], **III** · C_6H_6 [7] and $(C_6Me_6)Ti(AlCl_4)_2 \cdot C_6H_6$ (**V**) [6]

Parameter [a]	**I**	**II**	**III**	**III** · C_6H_6	**V**
Ti–C (ring)	2.32	2.298	2.49	2.50	2.50
Ti–centroid of ring	1.99	1.98	2.07	2.084	2.055
Ti–Cl	2.536	2.521	2.60	2.603	2.615
Al–Cl (bridge)	2.192	2.185	2.17	2.171	2.175
Al–Cl (outer)	2.056	2.079	2.08	2.076	2.100
Cl–Ti–Cl (bridge)	78.5	79.3	77.7–81.4	78.0	77.0
Cl–Al–Cl (bridge)	93.2	94.9	98.1	96.73	97.1
Cl–Al–Cl (outer)	117.1	116.8	115.1	113.25	114.9

[a] Average values of bond distances (Å) and valence angles (°).

Structures very similar to those found for **I** and **II** are also typical for a variety of $(\eta^6\text{-arene})Ti^{II}(AlX_4)_2$ (X = Cl,Br,I) complexes [5–7,27,28]. In all these structures the plane of arene or C_5H_5 or C_5Bz_5 ligands and the approximate plane of the bridging halogen atoms are nearly parallel. The change from Ti^{II} d^2 complex **III** to Ti^{III} d^1 complexes **I** or **II** brought about some shortening of Ti–Cl bonds whereas the Al–Cl bridging bonds were slightly elongated (see Table 5).

Nearly identical structures of the $Ti(AlCl_4)_2$ skeleton in the T^{III} and Ti^{II} complexes apparently account for practically identical equilibria (4), affording for given values of n and y equal values of x for L = C_6H_6, C_6Me_6, C_5H_5, and C_5Me_5.

$$(L)Ti(AlCl_4)_2 + nEt_yAlCl_{3-y}(y = 1\text{–}3) \rightleftharpoons (L)TiAl_2Cl_{8-x}Et_x + Et_{\acute{y}}AlCl_{3-\acute{y}}(y > \acute{y}) \quad (4)$$

These equilibria were established earlier on the base of ESR and UV-Vis investigations [3,4,20,29]. Their validity is limited only by different stability of products depending on the value of x (for C_6H_6 $x = 0$–2, for others $x = 0$–4). The direct proof of the validity of these equilibria was obtained recently by determining X-ray structure of the $(\eta^6\text{-}C_6Me_6)TiAl_2Cl_6Et_2$ complex, the expected product from the $(\eta^6\text{-}C_6Me_6)$-$TiAl_2Cl_8$ + 1.5 Et_3Al system [8]. Analogously, a virtual identity of the skeleton in **I** and **II** implies that equilibria (4) should also be valid for **I**.

3.2. *Formation of the $(\eta^5\text{-}C_5Bz_5)TiAl_2Cl_{8-x}Et_x$ complexes in the **III** + · C_5Bz_5H + nEt_3Al systems*

Redox reactions analogous to eqn. (3) between C_5Bz_5H and the **III** + 0.5, 1.5 or 4.0 Et_3Al systems afforded the paramagnetic complexes $(\eta^5\text{-}C_5Bz_5)Ti$-$Al_2Cl_{8-x}Et_x$ where x was, by analogy with other complexes fulfilling equilibria (4), equal or close to 1, 2 and 4, respectively. Their ESR and UV-Vis spectra and yields obtained from ESR analysis [20,29] are listed in Table 6. Both methods gave spectra which are very similar to those of the appropriate C_5Me_5 complexes but some differences are remarkable. The ESR *g*-factors are shifted to higher value by *ca.* 0.0011 for n increasing from 0 to 4 in both the **I**- and **IV**-based systems but the g-factors for the **I**-based complexes are constantly lower by *ca.* 0.0010. This would qualify the C_5Bz_5 ligand as more basic than C_5Me_5 which, however, is not realistic. The differences in ΔH are lower in C_5Bz_5 complexes for $n = 0.5$–4.0 and a_{Al} observed in **I** is only 0.54 mT compared to 0.575–0.580 mT in IV. The coupling constant $a(Ti_{7/2}) = 1.5$ mT, observable for $n = 4$, is the same in both the systems [4].

In the UV-Vis absorption spectra a shift of the most intense charge transfer band (A) to longer wavelengths with increasing value of n is at variance with the **II**- and **IV**-based systems. A weaker charge transfer band (B) forming a shoulder is shifted to shorter wavelengths in accordance with both the latter systems. A

TABLE 6. ESR and UV–Vis spectra of $(\eta^5\text{-}C_5Bz_5)Ti^{III}Al_2Cl_{8-x}Et_x$ complexes formed in the **III** + C_5Bz_5H + n Et_3Al systems [a]

n Et_3Al	g [b]	ΔH (mT)	No. of Et groups, (x) [c]	Yield (%) [d]	UV-Vis spectrum [e]		
					A	B	C
0	1.9685	$a_{Al} = 0.54$	0	70	403	490	650
0.5	1.9687	2.6	1	90	405	470	650
1.5	1.9690	1.85	2	90	410	460	650
4.0	1.9695	1.40	~ 4	65		[f]	

[a] The components mixed in the order C_5Bz_5H, (III) and Et_3Al (all in toluene solution); [b] additional ESR data: a (Ti, I = 7/2) = 1.5 mT for the system with $n = 4$ at 293 K; $g\| = 1.989$, $g\perp = 1.926$, $g_{av} = 1.968$ for all systems at 77 K; [c] assuming that equilibrium compositions of the systems are the same as in analogous systems with $(\eta^5\text{-}C_5H_{5-z}Me_z)TiAl_2Cl_{8-x}Et_x$ complexes [3,4]; [d] determined by ESR method [20] with accuracy of ±10%; [e] A,B: charge transfer bands, C: d-d transition; $\epsilon(A) = 1800$ cm^2 mmol^{-1}, B shoulder of lower intensity; $\epsilon(C) = 150$ cm^2 mmol^{-1} (values of ϵ for the system with $n = 1.5$). [f] Continuous absorption increasing in intensity to shorter wavelengths precluded the determination of λ_{max}.

weak and broad d–d transition (C) did not show observable shifts to longer wavelengths as found in the above systems [4]. This, in some respects different behaviour of the C_5Bz_5 complexes, shows that the effect of benzyl substituents at the cyclopentadienyl ligand cannot be accounted for only in terms of the electron donation effect which was well documented by the dependences of spectroscopic parameters in the series of $C_5H_{5-z}Me_z$ ($z = 0$–5) complexes [4].

Yields of $(\eta^5\text{-}C_5Bz_5)TiAl_2Cl_{8-x}Et_x$ complexes were nearly quantitative for $n = 0.5$ ($x = 1$) and $n = 1.5$ ($x = 2$) but lower for $n = 0$ (see preparation of **I**) and for $n = 4$. In the latter case the expected $(\eta^5\text{-}C_5Bz_5)TiAl_2Cl_4Et_4$ complex is partially decomposed to a diamagnetic byproduct which behaviour was also found for the analogous $C_5H_{5-z}Me_z$ complexes [4].

The $(\eta^5\text{-}C_5Bz_5)TiAl_2Cl_{8-x}Et_x$ complexes thus generally behave analogously to the $(\eta^5\text{-}C_5H_{5-z}Me_z)TiAl_2Cl_{8-x}Et_x$ ($z = 0$–5; $x = 0$–4) complexes and as follows from the structure of **I** no steric hindrance is imposed by the bulky C_5Bz_5 ligand. On the other hand, the benzyl groups influence the electronic Ti-ligand interactions in such a way that electron donation effect of Bz groups cannot be estimated from comparison of spectroscopic (ESR and UV-Vis) parameters of the C_5Bz_5 complexes with those of the $C_5H_{5-z}Me_z$ complexes. The stability of **I** and the order of Hammett's constants for Bz and Me groups [30] allow us to estimate the electronic property of C_5Bz_5 ligand to be similar to C_5HMe_4 or $C_5H_2Me_3$ ligands.

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