# DIMERIC STRUCTURES OF Cp'TiCl<sub>2</sub> COMPOUNDS WITH BULKY SUBSTITUENTS AT THE CYCLOPENTADIENYL RINGS

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The complexes  $[(\eta^5 - C_5 Me_4 Ph)TiCl(\mu-Cl)]_2$  (1) and  $[(\eta^5 - C_5 Bn_5)TiCl(\mu-Cl)]_2$  (2) (Bn = benzyl) were obtained by the reaction of TiCl<sub>3</sub> and the corresponding alkali metal cyclopentadienides in a THF-toluene mixture. The X-ray diffraction single-crystal analysis revealed that both compounds form centrosymmetric dimers bridged *via* a pair of chloride ligands. Compound 1 crystallizes in the monoclinic space group  $P2_1/n$  (No. 14; a = 11.387(3) Å, b = 16.496(2) Å, c = 8.383(2) Å,  $\beta = 110.786(15)^\circ$ , V = 1 472.2(6) Å<sup>3</sup>, Z = 2), and compound 2 in the monoclinic space group  $P2_1/c$  (No. 14; a = 17.996(5) Å,  $\beta = 116.747(15)^\circ$ , V = 3 267.2(13) Å<sup>3</sup>, Z = 2). Common features of the structures differ only negligibly. The Ti–Ti distance (in 1 3.3345(11) Å, in 2 3.374(2) Å) is considerably shorter than in paramagnetic dimeric titanocene monochlorides (3.91–3.95 Å). The compounds are diamagnetic, probably due to spin-paired d<sup>1</sup> electrons.

**Key words:** Sandwich complexes; Metallocenes; Titanocenes; Titanium(III) complexes; Cyclopentadienyl ligands; Chloride bridges; Crystal structures.

The cyclopentadienyltitanium(III) dichloride complexes of general formula  $[(\eta^5-C_5H_{5-n}Me_n)-TiCl_2]$  (n = 0-5) are purple amorphous solids which are insoluble in non-polar solvents<sup>1-6</sup>. They dissolve in coordinating solvents like THF to give pale green-blue solutions which, surprisingly, do not show EPR signals although the mononuclear nature of the complexes has been proved. Evaporation of the coordinating solvent restores the purple solids<sup>6</sup>. The X-ray crystal analysis revealed that the complex  $[(\eta^5-C_5H_5)TiCl_2(THF)_{1.5}]$  is an equimolar mixture of the four- and five-coordinate complexes  $[(\eta^5-C_5H_5)TiCl_2(THF)]$  and  $[(\eta^5-C_5H_5)TiCl_2(THF)_2]$  (ref.<sup>7</sup>); the composition of the  $[(\eta^5-C_5Me_5)TiCl_2(THF)]$  complex has also been well established<sup>5</sup>. Enlarging the size and/or lowering the basicity of the ancillary cyclopentadienyl ligand in transition metal complexes is known to decrease their nuclearity as it is exemplified by polymeric  $[(\eta^5-C_5H_5)RhCl_2]_n$  and dimeric  $[(\eta^5-C_5Me_5)RhCl_2]_2$  (ref.<sup>8</sup>). In the series of titanium compounds  $[(\eta^5-C_5H_5-nMe_n)TiCl_2]$  (n = 0-5), the change of nuclearity has not been

observed although the Lewis acidity at the titanium centre is considerably decreased by the electron donation effect of methyl groups at the cyclopentadienyl (Cp) ligands<sup>6</sup>.

In this paper we describe the syntheses and crystal structures of  $[(\eta^5-C_5Me_4Ph)TiCl(\mu-Cl)]_2$  (1) and  $[(\eta^5-C_5Bn_5)TiCl(\mu-Cl)]_2$  (2) (Bn = benzyl), the first dimeric compounds in the cyclopentadienyltitanium(III) dichloride series.

### EXPERIMENTAL

#### General

A high-vacuum glass technique was used for the manipulation of all reagents and the syntheses. Breakable seals were used to connect all-sealed reaction ampoules and measuring cuvettes. Tetrahydrofuran (THF), 2-methyltetrahydrofuran (MTHF), diethyl ether and toluene were purified over LiAlH<sub>4</sub> and subsequently stored as solutions of dimeric titanocene  $[(\mu-\eta^5:\eta^5-C_{10}H_8)]{(\eta^5-\eta^5-C_{10}H_8)}$  $(C_5H_5)_2Ti(\mu-H)_2$  (ref.<sup>9</sup>). Titanium tetrachloride was distilled over copper turnings and used as a 0.5 M solution in toluene. Butyllithium (1.6 M solution in hexanes, Fluka) was degassed and distributed into ampoules under vacuum. The paraffin oil of the potassium hydride suspension (Fluka) was replaced by hexanes. 2,3,4,5-Tetramethylcyclopent-2-en-1-one<sup>10</sup>, 1,2,3,4,5-pentabenzylcyclopentadiene<sup>11</sup> and potassiumpentabenzylcyclopentadienide<sup>12</sup> were prepared according to literature. Titanium trichloride was freshly prepared by reacting equimolar amounts of  $TiCl_4$  in toluene and butyllithium in hexanes. KBr pellets were prepared in a glovebox Labmaster 130 (mBraun) under purified nitrogen and were measured in an air-protecting cuvette on a Mattson Galaxy 2020 infrared spectrometer. Mass (EI) spectra were measured on a JEOL D-100 spectrometer at 70 eV. Samples in capillaries were opened and inserted into a direct inlet under argon. Mass (FD) spectra were obtained on a Varian MAT 711 spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Varian VXR-400 spectrometer (400 and 100 MHz, respectively) in  $C_6 D_6$  at 25 °C. Chemical shifts ( $\delta$ -scale) were referenced to the solvent signal ( $\delta_{\rm H}$  7.15 ppm,  $\delta_{\rm C}$  128.0 ppm). UV-VIS spectra were measured in the range 280–2 400 nm on a Varian Cary 17D spectrometer using all-sealed quartz cuvettes (Hellma d = 0.1 and 1.0 cm).

### 1,3,4,5-Tetramethyl-2-phenylcyclopenta-1,3-diene

A solution of phenyllithium was prepared from lithium (4.2 g, 0.61 mol) which was cut into small pieces and bromobenzene (48.7 g, 0.31 mol) in dried diethyl ether (400 ml). The solution was cooled down to 0 °C and a solution of 2,3,4,5-tetramethylcyclopent-2-en-1-one (31.9 g, 0.23 mol) in diethyl ether (100 ml) was gradually added. The mixture was then refluxed for two hours. After cooling to room temperature, the reaction mixture was hydrolyzed with a 10% aqueous NH<sub>4</sub>Cl solution (300 ml) and subsequently with dilute hydrochloric acid. The ether phase was separated and the aqueous phase was extracted several times with ether. The combined ether extracts were acidified with 10 ml of concentrated hydrochloric acid and the mixture was stirred for 4 h. The solution was neutralized with NaHCO<sub>3</sub> and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Pale orange 1,3,4,5-tetramethyl-2-phenylcyclopenta-1,3-diene was obtained by distillation at 94–96 °C at 1.73 kPa. Yield 32.5 g (71%) (*cf.* ref.<sup>13</sup>). Mass spectrum (FD-MS), m/z: M<sup>+</sup> 198; the sample contained small amounts of the HCl adduct (234) and biphenyl as impurities. IR spectrum (thin film, cm<sup>-1</sup>, transmission (%)): 480 (92), 527 (90), 575 (90), 633 (89), 700 (52), 739 (78), 754 (70), 766 (69), 909 (91), 980 (88), 1 072 (85), 1 130 (90), 1 177 (92), 1 377 (76), 1 443 (64), 1 493 (67), 1 599 (75), 2 857 (64), 2 868 (67), 2 913 (59), 2 924 (60), 2 965 (58), 3 027 (77), 3 057 (80), 3 077 (82).

Di- $\mu$ -chlorobis[chloro( $\eta^5$ -2,3,4,5-tetramethyl-1-phenylcyclopentadienyl)titanium(III)], [( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>Ph)TiCl( $\mu$ -Cl)]<sub>2</sub> (1)

Titanium tetrachloride (379 mg, 2 mmol) in 20 ml of toluene was reduced by butyllithium in hexanes (1.3 ml, 2.08 mmol). The brown suspension was stirred for 20 min and then a clear solution of freshly prepared Li(C<sub>5</sub>Me<sub>4</sub>Ph), made from C<sub>5</sub>HMe<sub>4</sub>Ph (400 mg, 2 mmol) and butyllithium (2.1 mmol), in 50 ml of THF was added to the TiCl<sub>3</sub> suspension. The colour turned to brown and did not change after heating to 90 °C for 48 h. After cooling to room temperature, the solvent was removed, the residue was washed with hexanes and finally recrystallized from toluene. The yield of brown crystals of 1 was approximately 400 mg (63%). IR spectrum (KBr), cm<sup>-1</sup>: 2 955 (m), 2 926 (s), 2 863 (m), 1 601 (m), 1 507 (m), 1 479 (m), 1 445 (m), 1 381 (s), 1 076 (m), 1 024 (m), 762 (vs), 702 (vs), 451 (m), 432 (s). UV-VIS, nm (toluene, 23 °C): 340 (sh) < 410 >> 500 (sh)  $\approx$  580 (sh); (MTHF, 23 °C): 335 >> 480 (sh)  $\approx$  660. EPR (toluene or MTHF, 25 to -130 °C): no signal attributable to 1. Mass spectrum (EI) (direct inlet, 200 °C), m/z (%): 630 (M<sup>+•</sup>, 2.4); 319 (10); 318 (10); 317 (45); 316 (20); 315  $([M/2]^+, 65); 314 (9); 313 (6); 282 (14); 281 (42); 280 ([M/2 - C1]^+, 44); 279 (100); 278 (26); 277$ (45); 276 (13); 275 (26); 274 (6); 265 (7); 264 (7); 263 (13); 262 (9); 261 (6); 198 (9); 197 (30); 196 (8); 182 (14); 181 (18); 180 (5); 179 (8); 178 (8); 167 (18); 166 (20); 165 (34); 155 (10); 153 (7); 152 (10); 141 (10); 128 (8); 115 (13); 91 (27). <sup>1</sup>H NMR spectrum: 2.069 s, 12 H (4 CH<sub>3</sub>); 2.161 s, 12 H  $(4 \text{ CH}_3)$ ; 7.026 m, 10 H (2 C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C NMR spectrum: 14.43 q; 15.72 q; 127.13 d; 128.64 d; 132.13 d; 136.37 s; 137.80 s; 140.83 s.

## Di- $\mu$ -chlorobis[chloro( $\eta^5$ -pentabenzylcyclopentadienyl)titanium(III)], [( $\eta^5$ -C<sub>5</sub>Bn<sub>5</sub>)TiCl( $\mu$ -Cl)]<sub>2</sub> (2)

A suspension of TiCl<sub>3</sub> (2 mmol) in toluene (20 ml) was prepared as described above. A red solution of pentabenzylcyclopentadienylpotassium, made from C<sub>5</sub>HBn<sub>5</sub> (1.03 g, 2 mmol) and an excess of potassium hydride in THF (30 ml), was added to the TiCl<sub>3</sub> suspension at room temperature. After a day at room temperature, the solution was cooled to 5 °C. Light blue crystals of  $[Li(THF)_2(\mu-Cl)_2-$ TiCl<sub>2</sub>(THF)<sub>2</sub>] (approximately 300 mg, 31%) crystallized out of the pale brown reaction mixture. The identity of [Li(THF)<sub>2</sub>(u-Cl)<sub>2</sub>TiCl<sub>2</sub>(THF)<sub>3</sub>] was confirmed by X-ray crystallography and lithium atom absorption spectroscopy (calculated 1.43%, found 1.35% Li). The mother liquor was reduced to half volume and put again to 5 °C. Compound 2 crystallized as very thin dark green plates. Further crystals were obtained by repeated reducing the volume of the solution. The overall yield of green crystalline 2 was 30 mg (2.4%). Similar low yields were obtained in three reproduced experiments.  $[(\eta^5-C_5Bn_5)TiCl(\mu-Cl)]_2$  (2): UV-VIS, nm (toluene, 23 °C): 350 (sh) < 415 >> 568; (MTHF, 23 °C): 310 > 460 (sh) > 640. EPR (toluene or MTHF, 23 to -196 °C): no signal attributable to 2. IR spectrum (KBr), cm<sup>-1</sup>: 3 104 (w), 3 084 (m), 3 063 (m), 3 028 (s), 2 930 (w), 2 918 (w), 1 603 (s), 1 584 (w), 1 495 (s), 1 451 (s), 1 182 (vw), 1 155 (vw), 1 076 (m), 1 030 (m), 795 (vw), 733 (vs), 696 (vs), 673 (vw), 588 (w), 480 (m), 461 (w), 444 (m). Mass spectrum (EI) (direct inlet, 300 °C), m/z (%): 633 ([M/2]<sup>+</sup>, 6); 596 (8); 543 (10); 542 (7); 541 (13); 516 (6); 515 (7); 514 (16); 510 (5); 505 (5); 423 (6); 422 (5); 421 (10); 332 (5); 331 (10); 330 (15); 265 (6); 255 (9); 254 (9); 252 (8); 241 (11); 239 (5); 215 (5); 167 (8); 165 (6); 92 (9); 91 (100); 65 (6). NMR spectra were not measured because of negligible solubility of 2 in  $C_6D_6$ .

### X-Ray Crystallography

A brown prismatic crystal of **1** and a green thin plate crystal of **2** were mounted into Lindemann glass capillaries in a glovebox containing purified nitrogen. Intensities were collected on a Philips PW1100 four-circle diffractometer (sealed tube, graphite monochromator, Mo anode,  $\lambda = 0.71069$  Å) at room temperature. The structures of **1** and **2** were solved by iterative symbolic addition (ISA,

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ref.<sup>14</sup>) and refined with full-matrix least squares based on  $F^2$  applying a variance-based weighting scheme (SHELXL93, ref.<sup>15</sup>). All non-hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were included in the refinement on calculated positions using a riding model. The torsion angle for the methyl groups in **1** was allowed to refine. ORTEP was used to draw the representations of **1** and **2** (ref.<sup>14</sup>). Crystal and refinement data for **1** and **2** are summarized in Table I. The positional and isotropic equivalent temperature parameters and anisotropic thermal parameters of **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre.The supplementary material is available from the author (G. S.) either in printed form or in files on diskette. The data are stored having the CIF and FCF standard of the International Union of Crystallography.

TABLE I

Parameters	1	2
Empirical formula	C <sub>30</sub> H <sub>34</sub> Cl <sub>4</sub> Ti <sub>2</sub>	C <sub>80</sub> H <sub>70</sub> Cl <sub>4</sub> Ti <sub>2</sub>
Molecular weight	632.17	1 268.96
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
Unit cell dimensions:		
<i>a</i> , Å	11.387(3)	18.967(5)
b, Å	16.496(2)	10.719(10)
<i>c</i> , Å	8.383(2)	17.996(5)
β, °	110.786(15)	116.747(15)
Volume, Å <sup>3</sup>	1 472.2(6)	3 267.2(13)
Ζ	2	2
$\rho_{calc}$ , g cm <sup>-1</sup>	1.426	1.290
$\mu$ , mm <sup>-1</sup>	0.924	0.453
F(000)	652	1 324
Crystal size, mm <sup>3</sup>	$0.55\times0.5\times0.4$	$0.6 \times 0.55 \times 0.1$
$\theta$ range for data collection, $^\circ$	3–26	3–23
Reflections collected	2 816	4 035
Unique reflections; R <sub>int</sub>	2 639; 0.025	3 899; 0.018
Data; restraints; parameters	2 638; 0; 169	3 898; 0; 390
Final $R_1$ ; $wR_2$ $(I > 2\sigma(I))$	0.0400; 0.0930	0.0534; 0.0922
Final $R_1$ ; $wR_2$ (all data)	0.0469; 0.1000	0.0685; 0.1034
Goodness-of-fit on $F^2$	1.099	1.144
Largest peak; hole, e $Å^{-3}$	0.321; -0.456	0.223; -0.234

Crystal and structure refinement data for  $[(\eta^5-C_5Me_4Ph)TiCl(\mu-Cl)]_2(1)$  and  $[(\eta^5-C_5Bn_5)TiCl(\mu-Cl)]_2(2)$ 

### **RESULTS AND DISCUSSION**

The complexes di- $\mu$ -chlorobis[chloro( $\eta^{5}$ -2,3,4,5-tetramethyl-1-phenylcyclopentadienyl)titanium(III)] (1) and di- $\mu$ -chlorobis[chloro( $\eta^{5}$ -pentabenzylcyclopentadienyl)titanium(III)] (2) were prepared from TiCl<sub>3</sub> and the corresponding alkali metal cyclopentadienide in a mixture of THF and toluene (Eq. (1)).



Compound **1** was obtained in 63% yield at the 1 : 1 molar ratio of the reagents. This is comparable to the yield of  $[(\eta^5-C_5Me_4Ph)_2TiCl]$  which was obtained at the 1 : 2 molar ratio in 71% yield<sup>16</sup>. In contrast, compound **2** was obtained in a very low yield of 2%. This yield was not increased either by an increase in the  $(C_5Bn_5)K/TiCl_3$  ratio or by prolonged heating of the reaction mixture to 60 °C. Instead, the pale blue complex  $[Li(THF)_2(\mu-Cl)_2TiCl_2(THF)_2]$  was obtained in yields of about 30% and its structure was established by single-crystal X-ray diffraction analysis<sup>17</sup>. The reason for the scarce formation of **2** probably lies in a titanium-catalyzed decomposition of  $C_5Bn_5K$  leading to perbenzylcyclopentadienyl radicals. The products of hydrogen transfer between the  $C_5Bn_5$  radicals ( $C_{40}H_{36}$  and  $C_{40}H_{34}$ ) were found by MS spectra in the oil present in the solid residue after complete evaporation of the reaction mixture. The LiCl formed in the reduction of TiCl<sub>4</sub> with butyllithium is a more efficient coordination agent for  $[TiCl_3(THF)_3]$  than the strongly ionic KCl which is also present in the system.

The dimeric structure of brown-green 1 and green 2 in the solid state and in toluene solutions follows from X-ray crystal diffraction analysis (*vide infra*) and from the persistence of the colour of the solid compounds in the solution. In the gas phase, the presence of the molecular ion m/z 630 of 1 shows that the dimer is stable up to 200 °C. Compound 2 requires a higher temperature of evaporation (300 °C) and thus only the ions of a dissociated monomer were observed. The solutions of both the compounds in toluene or MTHF are silent in EPR spectroscopy. In toluene, the antiferromagnetic interaction is exerted by the d<sup>1</sup> electrons at both titanium atoms in 1 and 2, forming an electronic singlet state. In MTHF solutions, the electronic absorption spectra indicate the coordination of MTHF to the monomeric species since a charge transfer band observable at 400 nm in the toluene solutions of the dimers disappears and a low-intensity band of likely d–d transition is well developed with  $\lambda_{max}$  at 660 nm for 1 and at 640 nm for 2. A very similar behaviour was observed for highly methyl substituted Cp'TiCl<sub>2</sub>

compounds<sup>6</sup>. The absence of EPR spectra in MTHF solutions of all these compounds may result from their short relaxation time. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **1** are compatible with the proposed structure, those of **2** were not measured because of low solubility of the compound in  $C_6D_6$ .

### Molecular Structures of 1 and 2

The X-ray diffraction analysis of  $[(\eta^5-C_5Me_4Ph)TiCl(\mu-Cl)]_2$  (1) and  $[(\eta^5-C_5Bn_5)TiCl(\mu-Cl)]_2$  (2) revealed that both of them form chloride-bridged centrosymmetric dimers. ORTEP drawings of 1 and 2 with the atom labelling schemes are shown in Figs 1 and 2. Selected bond distances and angles are compiled in Tables II and III.

The planar bridging skeletons in **1** and **2** form almost perfect squares. The small differences in the bridging bond angles lead to a slight, but significant increase in the non-bonding Ti–Ti distance from 3.3345(11) Å in **1** to 3.374(2) Å in **2**. These Ti–Ti distances are significantly shorter than the corresponding distances in chloride-bridged titanocene dimers  $[(\eta^5-C_5H_{5-n}Me_n)_2Ti(\mu-Cl)]_2$  (n = 0-2) (refs<sup>18,19</sup>) and the fulvalene complex  $[(\mu-\eta^5:\eta^5-C_{10}H_8){(\eta^5-C_5H_5)_2Ti(\mu-Cl)}_2]$  (ref.<sup>20</sup>). The comparison of common geometric parameters of **1**, **2** and the above compounds (Table IV) shows that the Ti–Cl bridging bond distances in **1** and **2** are shorter by about 0.1 Å. The outer Ti–Cl bond distances in **1** (2.2654(9) Å) and **2** (2.269(2) Å) are also rather short. For instance, in  $[(\eta^5-C_5H_5)TiCl_2(THF)_{1.5}]$  they range 2.310(1)–2.370(2) Å (ref.<sup>7</sup>) and in  $[TiCl_3(THF)_3]$  2.343(1)–2.380(1) Å (ref.<sup>21</sup>). In monomeric titanocene (Ti(IV) and Ti(III)) chlorides, where the Ti atom is tetrahedrally or trigonally coordinated, the shortest Ti–Cl bond has been so far found in  $[(\eta^5-C_5HMe_4)_2TiCl]$  being 2.316(4) Å (ref.<sup>22</sup>).

The Ti–CE distances (CE, center of the cyclopentadienyl ring) in **1** and **2** are shorter than those in[ $(\mu-\eta^5:\eta^5-C_{10}H_8)$ { $(\eta^5-C_5H_5)_2$ Ti $(\mu-Cl)$ }] and [ $(\eta^5-C_5H_3Me_2)_2$ Ti $(\mu-Cl)$ ]<sub>2</sub> (Table IV). The Ti–CE distances in monomeric titanocene chlorides are generally discernibly longer, *e.g.*, [ $(\eta^5-C_5Me_5)_2$ TiCl] (average 2.06(2) Å) (ref.<sup>23</sup>), [ $(\eta^5-C_5HMe_4)_2$ TiCl] (average 2.031(9) Å) (ref.<sup>22</sup>) or [ $(\eta^5-C_5Bn_5)(\eta^5-C_5H_5)$ TiCl] (Ti–CE(Bn) 2.042(4) Å;



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Selected bond distances (A	Å) and angles (°) for $[(\eta^5)$	$-C_5Me_4Ph)TiCl(\mu-Cl)]_2$ (1)
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Distances				
Ti1–Ti1 <sup>a</sup>	3.3345(11)	Ti1-CE1	2.008(5)	
Ti1-Cl1	2.4010(9)	Ti1–Cl1 <sup>a</sup>	2.3962(10)	
Ti1-Cl2	2.2654(9)			
Ti1-C1	2.344(3)	Ti1-C2	2.321(3)	
Ti1–C3	2.306(3)	Ti1–C4	2.362(3)	
Ti1–C5	2.385(2)			
C1–C2	1.427(4)	C1-C11	1.483(4)	
C1C5	1.430(3)	C2–C21	1.501(4)	
C2–C3	1.420(4)	C3–C31	1.499(4)	
C3–C4	1.423(4)	C4–C41	1.509(4)	
C4–C5	1.403(4)	C5-C51	1.494(4)	
Angles				
Ti1 <sup>a</sup> -Cl1-Ti1	88.07(3)	Cl1 <sup>a</sup> -Ti1-Cl1	91.93(3)	
CE1-Ti1-Cl1	115.5(7)	CE1-Ti1-Cl1 <sup>a</sup>	117.47(11)	
CE1-Ti1-Cl2	122.6(5)	CE1-Ti1-Ti1 <sup>a</sup>	129.9(6)	
Cl2-Ti1-Cl1	101.09(4)	Cl2-Ti1-Cl1 <sup>a</sup>	102.90(3)	

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: -x + 1, -y, -z + 1.



FIG. 2 ORTEP drawing (30% probability level) of  $[(\eta^5-C_5Bn_5)TiCl(\mu-Cl)]_2$ (2) with the atom labelling scheme Ti–CE(Cp) 2.034(4) Å) (ref.<sup>12</sup>). Only the  $[(\eta^5-C_5Bn_5)Ti(AlCl_4)_2]$  complex shows a slightly shorter Ti–CE distance of 1.99(2) Å (ref.<sup>11</sup>). The comparison of both the Ti–CE and Ti–Cl distances in **1** and **2** with those of similar compounds shows that the strength of bonding depends mainly on the Lewis acidity induced at the titanium atom by the electron-releasing chloride ligand. The coordination number of the titanium center affects the bonding distances to a smaller extent, as it is exemplified in the THF-adducts  $[(\eta^5-C_5H_5)TiCl_2(THF)_n]$  where the Ti–CE bond distance increases from 2.014(13) Å for n = 1 to 2.059(8) Å for n = 2 and the same trend appears with the Ti–Cl bonds (ref.<sup>7</sup>).

The cyclopentadienyl rings as well as the phenyl rings in **1** and **2** are planar within the experimental errors. The torsion angle between both rings in **1** is in the expected range  $(49.87(11)^\circ)$ . The methyl carbon atoms and the pivotal carbon atom of the phenyl

	Distances				
	Ti1–Ti1 <sup>a</sup>	3.374(2)	Ti1–CE1	2.018(4)	
	Ti1–Cl1	2.403(2)	Ti1–Cl1 <sup>a</sup>	2.4010(14)	
	Ti1–Cl2	2.269(2)			
	Ti1–C1	2.331(4)	Ti1–C2	2.348(4)	
	Ti1–C3	2.391(4)	Ti1–C4	2.376(4)	
	Ti1–C5	2.317(4)			
	C1–C2	1.413(6)	C1–C10	1.501(6)	
	C1–C5	1.426(6)	C2-C20	1.516(6)	
	C2–C3	1.421(6)	C3–C30	1.497(6)	
	C3–C4	1.427(5)	C4–C40	1.518(6)	
	C4–C5	1.426(6)	C5–C50	1.504(5)	
Angles					
	Ti1 <sup>a</sup> -Cl1-Ti1	89.23(5)	Cl1 <sup>a</sup> -Ti1-Cl1	90.77(5)	
	CE1-Ti1-Cl1	114.43(5)	CE1-Ti1-Cl1 <sup>a</sup>	116.44(5)	
	CE1-Ti1-Cl2	123.59(5)	CE1-Ti1-Ti1 <sup>a</sup>	127.69(5)	
	Cl2-Ti1-Cl1	99.36(6)	Cl2-Ti1-Cl1 <sup>a</sup>	106.27(6)	
	C1C10C11	115.0(4)	C2-C20-C21	118.2(3)	
	C3-C30-C31	114.9(3)	C4-C40-C41	114.5(4)	
	C5-C50-C51	115.9(4)			

TABLE III Selected bond distances (Å) and angles (°) for  $[(\eta^5-C_5Bn_5)TiCl(\mu-Cl)]_2$  (2)

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: -x, -y, -z.

group deviate only slightly from the cyclopentadienyl ring, farther away from the Ti center (0.052(4) to 0.123 (4) Å). These low values do not indicate an appreciable steric hindrance introduced by the ring substituents. In 2, four of the five benzyl substituents are directed away from the Ti atom, one benzyl group is inclined towards the Ti atom. The C(Cp)-CH<sub>2</sub>-C(Ph) bond angles for the upward-directed benzyl groups fall in the narrow range of 114.5(4) to 115.9(4)°. This angle for the downward-directed benzyl group is significantly larger (118.2(3)°). Similar values for the C(Cp)-CH<sub>2</sub>-C(Ph) bond angles in the up or down position were found in other  $(\eta^5-C_5Bn_5)Ti$  complexes in the Ti(II-IV) oxidation states<sup>11,12</sup>. The methylene carbon atoms of the upward-orientated benzyl substituents are placed away from the cyclopentadienyl ring plane farther from the Ti atom (maximum for C10 0.152(7) Å). The methylene carbon atom C50 of the downward-orientated benzyl group deviates towards the Ti atom (0.071(7) Å). These values do not imply an appreciable steric congestion, too. Small deviations, with a maximum of 0.09 Å, were also observed in a sterically non-hindered  $[(\eta^5-C_5Bn_5)Ti(AlCl_4)_2]$ where the benzyl groups form a crown configuration<sup>11</sup>. In the seriously crowded complexes  $[(\eta^5 - C_5 Bn_5)(\eta^5 - C_5 H_5)TiCl]$  and  $[(\eta^5 - C_5 Bn_5)(\eta^5 - C_5 H_5)TiCl_2]$ , the upward deviations are larger, 0.25 and 0.37 Å, respectively<sup>12</sup>. The phenyl group in 1 and the downward-oriented benzyl group of 2 are directed into the same space with respect to the bridging skeleton. Thus, this sterical screening of the Ti centre seems to prevent a further spatial bridging in these compounds. The electronic arguments cannot be applied as the permethylated complex  $[(\eta^5-C_5Me_5)TiCl_2]_n$  shows the same spatial bridg-

TABLE IV Comparison of the bond distances (Å) and angles (°) of the bridging moieties in the complexes 1, 2,  $[(\eta^5-C_5H_3Me_2)_2Ti(\mu-Cl]_2 (\mathbf{A}) (ref.^{19}) and [(\mu-\eta^5:\eta^5-C_{10}H_8)\{(\eta^5-C_5H_5)_2Ti(\mu-Cl)\}_2] (\mathbf{B}) (ref.^{20})$ 

Atoms	1	2	Α	В
Distances				
Ti–Ti	3.3345(11)	3.374(2)	3.9155(8)	3.638
Ti-Cl (bridge)	2.4010(9)	2.403(2)	2.5425(7)	2.514(1)
	2.3962(10)	2.4010(14)	2.5412(7)	2.524(1)
Ti-Cl (terminal)	2.2654(9)	2.269(2)		
Ti-CE	2.008(5)	2.018(4)	2.077(2)	2.059
			2.064(2)	2.054
		Angles		
Ti–Cl–Ti	88.07(3)	89.23(5)	100.75(2)	92.47(3)
Cl-Ti-Cl	91.93(3)	90.77(5)	79.25(2)	81.29(4)

ing mode as all other less methyl substituted compounds of the series<sup>5,6</sup> and both the  $C_5Me_4Ph$  and  $C_5Bn_5$  ligands have similar electron donation properties as the  $C_5Me_5$  ligand<sup>11,12</sup>.

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