

# Novel Group 4b *ansa*-metallocene complexes with the shortest bridge: [1,1'-isopropylidene-3,3'-di-*t*.Bu-bis( $\eta^5$ -cyclopentadienyl)] Ti and Zr dichlorides<sup>1</sup>

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## Abstract

Reaction of [1,1'-isopropylidene-3,3'-di-*tert*.butyl-bis( $\eta^5$ -cyclopentadienide)] dilithium with TiCl<sub>3</sub>, followed by treatment with HCl, and ZrCl<sub>4</sub> in various solvent mixtures in the temperature range 0–50°C gives corresponding *ansa*-metallocene dichlorides as mixtures of the *anti*/*syn*-isomers, 1:1. The crystal and molecular structures of three of the four isomers were determined, i.e. *rac*(*anti*)-[1,1'-isopropylidene-3,3'-di-*tert*.butyl-bis( $\eta^5$ -cyclopentadienyl)]TiCl<sub>2</sub>, space group *B2/b*, *rac*(*anti*)-[1,1'-isopropylidene-3,3'-di-*tert*.butyl-bis( $\eta^5$ -cyclopentadienyl)]ZrCl<sub>2</sub>, space group *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>*, and *meso*(*syn*)-1,1'-[isopropylidene-3,3'-di-*tert*.butyl-bis( $\eta^5$ -cyclopentadienyl)]ZrCl<sub>2</sub>, space group *P2<sub>1</sub>/n*. © 1997 Elsevier Science S.A.

**Keywords:** Metallocenes; *ansa*-Metallocenes; Titanium; Zirconium; Crystal structure

## 1. Introduction

Spectacular advances in stereoregular  $\alpha$ -olefin polymerisation processes (for a recent review, see Ref. [1]) draw attention to the synthesis of novel *ansa*-metallocene complexes of the Group 4b elements. Although many compounds of this type have been synthesised, complexes with the shortest bridge, of one carbon atom, for which the molecular structures were reported, are still quite few [2–15].

Recently the X-ray structures of the *ansa*-metallocenes, Me<sub>2</sub>C(C<sub>3</sub>H<sub>4</sub>)<sub>2</sub>MCl<sub>2</sub> (M = Ti, Zr, and Hf) were reported [15], so the structural study of the *tert*.butyl-substituted analogues, [1,1'-isopropylidene-3,3'-di-*tert*.butyl-bis( $\eta^5$ -cyclopentadienyl)]MCl<sub>2</sub>, would allow one to elucidate the influence of the bulky substituents on the geometry of the strained Me<sub>2</sub>Ccp<sub>2</sub>M moiety.

## 2. Experimental details

All experimental procedures were performed in inert atmosphere or in vacuum. All the solvents were purified and dried by standard procedures, and saturated with Ar at room temperature. The <sup>1</sup>H NMR spectra were registered on a Bruker AC-200 instrument in CDCl<sub>3</sub> solution at r.t. if not specified otherwise. Elemental analyses were performed by the Service Central d'Analyse du CNRS, Vernaison, France. The details of the X-ray experiments are listed in Table 1, the atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms in **1a**, **2a**, and **2b** are listed in Tables 2–4. For **2b** hydrogen atoms were not located.

### 2.1. 2,2-Di-[3-(6,6-dimethylfulvenyl)]propane

Solution of the double bond shift isomers of 2,2-dicyclopentadienylpropane [16], 15.3 g, 89 mmol, in 80 ml of reagent-grade methanol was treated with reagent-grade acetone, 32 ml, 440 mmol, and pyrrolidine, 25 ml,

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<sup>1</sup> Dedicated to the memory of Professor Yu.T. Struchkov.

300 mmol, at r.t. In 10 min the reaction mixture warmed spontaneously. Then it was refluxed for 5 min and left for 24 h at ambient conditions. Then it was treated with 500 ml of water and 100 ml of ether, shaken, the organic layer separated, washed twice with 300 ml of 1% acetic acid, and twice with 300 ml of water. The solvent was removed and a bright yellow oil resulted, which turned crystalline in the refrigerator. Recrystallisation from a minimum amount of methanol gave analytically pure samples, m.p. 58 °C. Yield 20 g, 90%.  $C_{19}H_{24}$ , calcd.: C, 90.58; H, 9.42%; found: C, 90.30; H, 9.11%.

$^1H$  NMR,  $\delta$ (ppm): 6.44–6.48 (m, 2H), 6.37–6.38 (m, 2H), 6.18–6.20 (m, 2H), 2.134 (s, 6H), 2.115 (s, 6H), 1.445 (6H).

## 2.2. [1,1'-Isopropylidene-3,3'-di-*t*.Bu-bis(cyclopentadienide)]Li<sub>2</sub>

Solution of 2,2-di-[3-(6,6-dimethylfulvenyl)]propane, 2.52 g, 0.01 mmol, in 50 ml of ether was treated at 0 °C with 10 ml of 2 M MeLi in ether, 0.02 mmol, under vigorous stirring. After all of the MeLi had been added, the cooling bath was removed, and the reaction mixture was left to warm at r.t. The yellow colour of the fulvene slowly disappeared during the next 24 h, and a snow-white free precipitate separated. The mother solution was removed, and the product was washed with 25 ml of ether and dried in vacuum. Yield 2.7 g, 80%, calcd. for an etherate  $C_{21}H_{30}Li_2 \cdot \frac{2}{3}Et_2O$ .

$^1H$  NMR, thf-*d*<sub>6</sub>: 5.49 (pseudotr, 2H), 5.34 (pstr,

2H), 1.44 (s, 6H), 1.05 (s, 18H), co-crystallised ether 3.39 (qu, 2.7H), 1.12 (tr, 4H).

## 2.3. [1,1'-Isopropylidene-3,3'-di-*t*.Bu-bis( $\eta^5$ -cyclopentadienyl)]TiCl<sub>2</sub>, **1a** / **1b**

Suspension of  $C_{21}H_{30}Li_2 \cdot \frac{2}{3}Et_2O$ , 0.01 mmol, in 50 ml of ether was added by small portions to a vigorously stirred suspension of TiCl<sub>3</sub>, 1.54 g, 0.01 mmol, in 50 ml of toluene at 0 °C for 1 h. Then the reaction mixture was stirred 12 h at r.t. The solid residue was separated, and clear blackish green solution was decanted and dried to give an almost-black solid. It was dissolved in 200 ml of hexane and treated with excess of saturated ethereal HCl, 50 ml. The solvent was removed in vacuum, resulting in a deep-green solid which was recrystallised from a minimum of hexane to give 1.6 g, 40% of dark-green needles **1a**, m.p. 190 °C.

$C_{21}H_{30}TiCl_2$ , calcd.: C, 62.86; H, 7.54%; found: C, 62.64; H 7.44%.

$^1H$  NMR,  $\delta$ (ppm): 6.76 (pstr, 2H), 5.51 (pstr, 2H), 5.35 (pstr, 2H), 1.75 (s, 6H), 1.32 (s, 18H).

After the separation of **1a** the mother solution was dried and the residue was dissolved in 10 ml of pentane. The solution was left to slowly evaporate at -10 °C. Dark-green polycrystalline **1b** separated after some time, 1 g, 25%, m.p. 160 °C. Found: C, 63.01; H, 7.80%.

$^1H$  NMR,  $\delta$ (ppm): 6.68 (pstr, 2H), 5.68 (pstr, 2H), 5.29 (pstr, 2H), 1.82 (s, 3H), 1.67 (s, 3H), 1.34 (s, 18H).

Table 1  
Details of the X-ray diffraction study of **1a**, **2a**, and **2b**

	<b>1a</b>	<b>2a</b>	<b>2b</b>
Formula	$C_{21}H_{30}TiCl_2$		$C_{21}H_{30}ZrCl_2$
FW	401.25		444.59
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$B2/b$	$P2_12_12_1$	$P2_1/n$
<i>a</i> (Å)	26.833(8)	9.374(6)	12.910(9)
<i>b</i> (Å)	25.718(8)	13.277(7)	19.924(7)
<i>c</i> (Å)	9.400(2)	16.826(6)	9.577(7)
$\gamma$ (deg)	100.91(2)		97.42(5)
<i>V</i> (Å) <sup>3</sup>	6369.6(2)	2094(2)	2442.8(3)
<i>Z</i>	12	4	4
$\rho$ (calcd) (g cm <sup>-3</sup> )	1.26	1.410	1.21
Diffractometer	KM-4	Enraf-Nonius CAD-4	KM-4
Radiation (graphite monochromator)	Mo K $\alpha$ ( $\lambda = 0.71069$ Å)		
Linear absorption coeff. (cm <sup>-1</sup> )	6.5	7.74	6.6
Scan type	$\theta-2\theta$	$\omega-2\theta$	$\theta-2\theta$
Scan range	$0.7 + 0.33 \tan \theta$	$0.8 + 0.345 \tan \theta$	$0.8 + 0.45 \tan \theta$
$\theta$ limits (deg)	6–28	1–25	2–28
No of data collected	4310	2123	4604
No of unique data collected	3085	2099	3830
No of unique data used ( $F_o$ ) <sup>2</sup> > 3 $\sigma$ ( $F_o$ ) <sup>2</sup>	1634	1649	2812
$R = \Sigma( F_o  -  F_c ) / \Sigma F_o $	0.061	0.035	0.078
$R_w = [\Sigma w( F_o  -  F_c )^2 / \Sigma w F_o^2]^{1/2}$	0.065	0.038	0.081

Table 2  
Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for two independent molecules **1a**

Atom	x	y	z	$U_{\text{eq}}^a$
Ti(1)	0.03217(1)	0.4035(1)	0.3267(2)	0.041
Ti(2)	0.500	0.250	0.2703(2)	0.057
Cl(1)	0.2592(1)	0.4238(1)	0.1790(3)	0.079
Cl(2)	0.3707(1)	0.3744(1)	0.1472(3)	0.084
Cl(3)	0.4752(1)	0.3095(2)	0.4347(3)	0.099
C(1)	0.3429(4)	0.4090(4)	0.6430(9)	0.065
C(2)	0.3142(3)	0.3648(4)	0.5525(9)	0.052
C(3)	0.2642(3)	0.3593(4)	0.5031(9)	0.050
C(4)	0.2539(3)	0.3227(4)	0.3893(9)	0.049
C(5)	0.3001(4)	0.3063(3)	0.364(1)	0.054
C(6)	0.3377(3)	0.3334(4)	0.461(1)	0.052
C(7)	0.2044(3)	0.2969(4)	0.332(1)	0.059
C(8)	0.2084(4)	0.2856(4)	0.168(1)	0.074
C(9)	0.1648(4)	0.3339(5)	0.351(1)	0.081
C(10)	0.1881(5)	0.2459(5)	0.412(1)	0.089
C(11)	0.3553(3)	0.4509(3)	0.5274(8)	0.044
C(12)	0.3974(3)	0.4532(4)	0.4300(9)	0.051
C(13)	0.3903(3)	0.4867(3)	0.3164(9)	0.045
C(14)	0.3422(4)	0.5013(4)	0.336(1)	0.059
C(15)	0.3217(4)	0.4787(4)	0.463(1)	0.055
C(16)	0.4283(4)	0.5089(4)	0.204(1)	0.065
C(17)	0.4034(5)	0.5092(5)	0.056(1)	0.092
C(18)	0.4713(4)	0.4808(6)	0.203(1)	0.095
C(19)	0.4490(6)	0.5678(7)	0.247(2)	0.120
C(20)	0.3898(5)	0.3956(5)	0.715(1)	0.075
C(21)	0.3075(5)	0.4263(6)	0.755(1)	0.087
C(22)	0.500(4)	0.250(4)	-0.056(1)	0.068
C(23)	0.4586(4)	0.2253(4)	0.057(1)	0.063
C(24)	0.4558(5)	0.1801(5)	0.129(1)	0.077
C(25)	0.4217(4)	0.1773(4)	0.246(1)	0.052
C(26)	0.4070(4)	0.2271(5)	0.248(1)	0.064
C(27)	0.4301(4)	0.2598(5)	0.136(1)	0.069
C(28)	0.3974(4)	0.1311(4)	0.336(1)	0.072
C(29)	0.3907(6)	0.1476(6)	0.488(1)	0.089
C(30)	0.4289(6)	0.0867(5)	0.330(2)	0.098
C(31)	0.3450(6)	0.1114(7)	0.273(2)	0.123
C(32)	0.5177(6)	0.2056(6)	-0.144(1)	0.101

$$^a U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$$

Analogously the reaction was performed in other solvent mixtures, see Scheme 1, at 0 and 50 °C. The crude reaction product, after treatment with HCl and evaporation of the solvent, was a 1:1 mixture of **1a/1b** with only minimum impurities, by  $^1\text{H}$  NMR.

#### 2.4. $[1,1'$ -Isopropylidene-3,3'-di-*t*-Bu-bis( $\eta^5$ -cyclopentadienyl)]ZrCl<sub>2</sub>, **2a** / **2b**

The analogous reaction between C<sub>21</sub>H<sub>30</sub>Li<sub>2</sub> ·  $\frac{2}{3}$ Et<sub>2</sub>O and ZrCl<sub>4</sub> was performed, in different solvent mixtures at 0 and 50 °C. Fractional crystallisation of the crude 1:1 mixture of **2a/2b**, by  $^1\text{H}$  NMR, from hexane–toluene 1:1 gave pure **2a**, bright yellow cubes, 1.7 g, 40%, m.p. 230 °C. C<sub>21</sub>H<sub>30</sub>ZrCl<sub>2</sub>, calcd.: C, 56.73; H, 6.80%; found: C, 56.91; H, 6.74%.

$^1\text{H}$  NMR,  $\delta$ (ppm): 6.49 (pstr, **2H**), 5.66 (pstr, **2H**), 5.51 (pstr, **2H**), 1.74 (s, **6H**), 1.29 (s, **18H**).

Table 3  
Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for **2a**

Atom	x	y	z	$U_{\text{eq}}^a$
Zr(1)	0.03931(7)	0.13312(5)	0.22331(4)	0.0275
Cl(1)	-0.1058(3)	-0.0068(2)	0.1764(1)	0.0519
Cl(2)	-0.1479(2)	0.2547(2)	0.2479(1)	0.0491
C(1)	0.3672(8)	0.1632(7)	0.2515(4)	0.0411
C(2)	0.2756(8)	0.1863(6)	0.1787(4)	0.0353
C(3)	0.2327(8)	0.1167(7)	0.1216(4)	0.0357
C(4)	0.1204(8)	0.1572(6)	0.0748(4)	0.0314
C(5)	0.0902(8)	0.2529(6)	0.1069(4)	0.0338
C(6)	0.1841(8)	0.2700(6)	0.1716(4)	0.0362
C(7)	0.0571(9)	0.1174(6)	-0.0025(4)	0.0355
C(8)	0.081(1)	0.0023(6)	-0.0099(5)	0.0445
C(9)	0.138(1)	0.1687(8)	-0.0717(5)	0.0595
C(10)	-0.1012(9)	0.1319(8)	-0.0106(5)	0.0496
C(11)	0.2538(8)	0.1181(6)	0.3049(4)	0.0331
C(12)	0.1553(8)	0.1739(6)	0.3532(4)	0.0344
C(13)	0.0439(9)	0.1096(5)	0.3785(4)	0.0331
C(14)	0.0694(9)	0.0161(6)	0.3433(4)	0.0353
C(15)	0.1971(9)	0.0191(6)	0.2980(5)	0.0413
C(16)	-0.0662(9)	0.1309(7)	0.4408(4)	0.0426
C(17)	-0.076(1)	0.2444(8)	0.4601(5)	0.0549
C(18)	-0.212(1)	0.0948(8)	0.4151(6)	0.0650
C(19)	-0.018(1)	0.0742(9)	0.5172(5)	0.0688
C(20)	0.4849(8)	0.0849(8)	0.2308(6)	0.0524
C(21)	0.4328(9)	0.2591(8)	0.2867(5)	0.0546

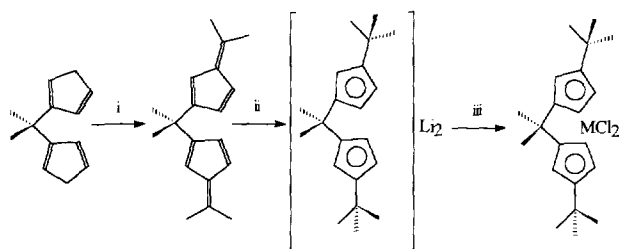
$$^a U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$$

After the separation of **2a** the mother solution was diluted with 5 ml of hexane. After 2 days at r.t. orange yellow crystals of **2b** separated, 1.3 g, 30%, m.p. 85 °C.

Table 4  
Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for **2b**

Atom	x	y	z	$U_{\text{eq}}^a$
Zr(1)	0.6839(1)	0.2184(1)	0.1509(1)	0.0426
Cl(1)	0.5670(4)	0.2666(2)	0.3016(5)	0.068
Cl(2)	0.8318(3)	0.1946(3)	0.3306(5)	0.081
C(1)	0.676(1)	0.1890(7)	-0.174(1)	0.044
C(2)	0.643(1)	0.1446(6)	-0.053(1)	0.037
C(3)	0.5457(9)	0.1515(7)	0.004(1)	0.042
C(4)	0.552(1)	0.1156(7)	0.133(1)	0.045
C(5)	0.655(1)	0.0918(7)	0.157(1)	0.050
C(6)	0.707(1)	0.1082(7)	0.046(2)	0.049
C(7)	0.463(1)	0.0976(8)	0.215(2)	0.057
C(8)	0.493(1)	0.0971(9)	0.372(2)	0.074
C(9)	0.374(1)	0.144(1)	0.185(2)	0.077
C(10)	0.424(2)	0.029(1)	0.165(2)	0.095
C(11)	0.714(1)	0.2516(7)	-0.087(1)	0.039
C(12)	0.6448(9)	0.3004(6)	-0.044(1)	0.037
C(13)	0.699(1)	0.3422(7)	0.060(1)	0.040
C(14)	0.802(1)	0.3143(7)	0.087(1)	0.045
C(15)	0.8109(9)	0.2592(7)	-0.002(1)	0.043
C(16)	0.666(1)	0.4086(7)	0.116(1)	0.046
C(17)	0.710(1)	0.4212(9)	0.265(2)	0.068
C(18)	0.549(1)	0.4160(9)	0.096(2)	0.068
C(19)	0.708(2)	0.4648(9)	0.028(2)	0.075
C(20)	0.768(1)	0.1544(9)	-0.236(2)	0.066
C(21)	0.585(1)	0.2018(9)	-0.289(2)	0.060

$$^a U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$$



**M = Ti - anti - 1a; syn - 1b; 1:1**

**Zr - anti - 2a; syn - 2b; 1:1**

Scheme 1. Legend: (i) acetone (2 equiv.), pyrrolidine, methanol, 24 h, 90%; (ii) MeLi (2 equiv.), ether, 0 to 25 °C, 24 h, 80%; (iii) (1) TiCl<sub>3</sub>, various solvent mixtures (ether, toluene, heptane), temp. range 0 to 50 °C, 6 to 12 h; (2) hexane, HCl-ether, isolable yield **1a** = 40%, **1b** = 25%; (iv) ZrCl<sub>4</sub>, various solvent mixtures, temp. range 0 to 50 °C, 6 to 12 h, isolable yield **2a** = 40%, **2b** = 30%.

Found: C, 57.11; H, 6.90%. <sup>1</sup>H NMR, δ(ppm): 6.48 (pstr, 2H), 5.73 (pstr, 2H), 5.51 (pstr, 2H), 1.79 (s, 3H), 1.69 (s, 3H), 1.30 (s, 18H).

### 3. Results and discussion

The incorporation of the Me<sub>2</sub>C bridge into the Group 4b metallocene dichloride unit leads to significant changes in the geometry of the sandwiches, as compared with the geometry of the parent Cp<sub>2</sub>MCl<sub>2</sub> molecules [15]. On the other hand, introduction into the

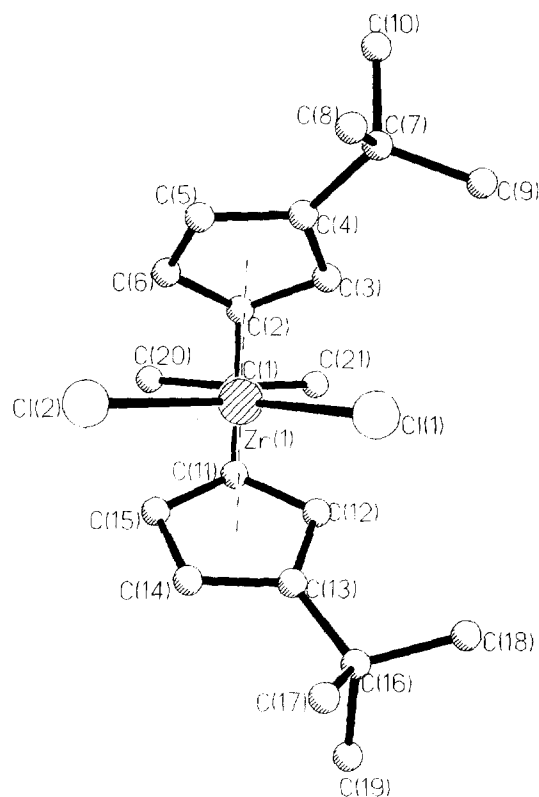


Fig. 1. General view of the molecules **2a** and **2b**. Hydrogen atoms are omitted for clarity; all the other atoms are drawn isotropic and of arbitrary magnitude.

Cp rings of bulky t.Bu substituents could eventually cause other geometric changes accompanying an increasing intramolecular tension.

Table 5  
Important bond distances (Å) in **1a**, **2a** and **2b**

	<b>1a</b>	<b>2a</b>	<b>2b</b>		<b>1a</b>	<b>2a</b>	<b>2b</b>
M-Cl(1)	2.312(4)	2.434(2)	2.418(5)	C(1)-C(20)	1.53(2)	1.56(1)	1.56(2)
	2.36(7)				1.55(9)		
M-Cl(2)	2.347(4)	2.420(2)	2.446(5)	C(2)-C(3)	1.40(1)	1.39(1)	1.44(2)
					1.34(2)		
M-C(2)	2.337(9)	2.443(7)	2.45(1)	C(2)-C(6)	1.41(1)	1.41(1)	1.38(2)
	2.32(5)				1.48(2)		
M-C(3)	2.40(1)	2.503(7)	2.51(1)	C(3)-C(4)	1.42(1)	1.42(1)	1.42(2)
	2.36(8)				1.42(2)		
M-C(4)	2.56(1)	2.632(7)	2.65(1)	C(4)-C(5)	1.40(1)	1.41(1)	1.40(2)
	2.5(1)				1.41(2)		
M-C(5)	2.48(1)	2.567(7)	2.55(1)	C(5)-C(6)	1.44(1)	1.42(1)	1.37(2)
	2.5(1)				1.42(2)		
M-C(6)	2.31(1)	2.430(8)	2.45(1)	C(4)-C(7)	1.47(2)	1.52(1)	1.52(2)
	2.32(9)				1.50(1)		
M-C(11)	2.334(9)	2.442(7)	2.45(1)	C(11)-C(12)	1.45(1)	1.44(1)	1.41(2)
M-C(12)	2.392(9)	2.500(7)	2.47(1)	C(11)-C(15)	1.39(1)	1.42(1)	1.41(2)
M-C(13)	2.547(8)	2.631(7)	2.63(1)	C(12)-C(13)	1.41(1)	1.41(1)	1.41(2)
M-C(14)	2.47(1)	2.563(7)	2.57(1)	C(13)-C(14)	1.42(1)	1.40(1)	1.44(2)
M-C(15)	2.32(1)	2.461(8)	2.48(1)	C(14)-C(15)	1.39(1)	1.50(1)	1.40(2)
C(1)-C(2)	1.51(2)	1.53(1)	1.56(2)	C(13)-C(16)	1.51(1)	1.50(1)	1.51(2)
	1.58(8)						
C(1)-C(11)	1.52(1)	1.51(1)	1.54(2)	C(1)-C(21)	1.54(2)	1.53(1)	1.52(2)

We undertook synthesis of a family of 3,3'-t.Bu-substituted *ansa*-metallocene dichlorides of Ti and Zr with the Me<sub>2</sub>C bridge. These were obtained via complexation of [1,1'-isopropylidene-3,3'-di-t.Bu-bis(cyclopentadienide)]Li<sub>2</sub>, see Scheme 1, along the lines of the reaction sequence reported in Ref. [17]. The final step produces 1:1 mixtures of the *syn*/*anti*-isomers, presumably because the reaction proceeds under non-equilibrium conditions. Fractional crystallisation gives pure, by <sup>1</sup>H NMR, *anti*-isomers as the first crop. From the mother solution less pure *syn*-isomers are isolated as the second crop. It should be noted that both Ti complexes are highly soluble in hydrocarbons, even in hexane and pentane. We obtained single crystals suitable for X-ray analysis for three of the four isomers, **1a**, **2a**, and **2b**, as described in Section 2. The general view of the molecules **2a** and **2b**, and the atom numbering scheme are presented in Fig. 1. The atomic configuration of **1a** molecule does not differ substantially from that of **2a**. Two crystallographically independent molecules of **1a** were found, one in general position, and the other on the C<sub>2</sub> crystallographic axis, the numbering for both is analogous to that of **2a**. The most important bond distances and angles of the molecules **1a**, **2a**, and **2b** are listed in Tables 5 and 6. As it could be expected, introduction of the t.Bu substituents caused evident changes in the M-C(cp) distances, which are for **1a** in the range 2.31–2.5 Å and for **2a** and **2b** in the range 2.43–2.65 Å. These distances are varying from 2.33 to 2.45 Å in Me<sub>2</sub>C(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>TiCl<sub>2</sub>, **4**, and from 2.445 to 2.56 Å in Me<sub>2</sub>C(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>ZrCl<sub>2</sub>, **5** [15]. Consequently the average M-C(cp) distance *d* is 0.04 Å greater in **1a** (2.42 Å) compared with **4** (2.38 Å), Table 7. Quite predictably, the average M-C(cp) distance in (*syn*)-[1,1'-isopropylidene-3,3'-di-isopropyl bis(η<sup>5</sup>-cyclopentadienyl)]TiCl<sub>2</sub>, **3**, is 2.40 Å [14]. For the Zr molecules, these values are 2.52 Å in **2a** and **2b**, and 2.50 Å in **5**. The longest M-C(cp) distance in **1a**, **2a**, and **2b** corresponds to the C-C(t.Bu) atoms of the rings. The perpendicular distance from M to the cp-plane *n* is

Table 6  
Important bond angles (deg) in **1a**, **2a** and **2b**

	<b>1a</b>	<b>2a</b>	<b>2b</b>
Cl(1)–M–Cl(2)	96.6(1)	98(1)	99.17(9)
C(2)–C(1)–C(11)	98.3(8)	96(1)	99.2(6)
C(3)–C(2)–C(6)	105.3(8)	109(1)	106.8(7)
C(2)–C(3)–C(4)	112.2(9)	112(1)	110.2(7)
C(3)–C(4)–C(5)	105.0(9)	104.4(9)	106.1(7)
C(4)–C(5)–C(6)	108.8(9)	111(1)	108.3(7)
C(2)–C(6)–C(5)	108.5(5)	103.6(9)	108.4(7)
C(12)–C(11)–C(15)	106.2(8)		106.4(7)
C(11)–C(12)–C(13)	108.0(8)		109.5(7)
C(12)–C(13)–C(14)	107.4(8)		106.4(7)
C(13)–C(14)–C(15)	107.7(9)		110.4(7)
C(11)–C(15)–C(14)	110.3(9)		107.3(7)

Table 7  
Comparative sandwich geometry characteristics of **2a**, **2a** and **2b**

	δ (deg) <sup>a</sup>	ϑ (deg) <sup>b</sup>	ψ (deg) <sup>c</sup>	<i>d</i> (Å) <sup>d</sup>	<i>n</i> (Å) <sup>e</sup>	Ref.
<b>1a</b>	70.3	98	8	2.42	2.08	this work
	70.4	96	10			
			11			
<b>3</b>	67.8	96.6	4.8	2.40	2.05	[14]
<b>4</b>	66.9	96.7		2.38	2.056	[15]
<b>2a</b>	73.9	99	8.0	2.52	2.21	this work
			8.8			
<b>2b</b>	73.4	99	10	2.52	2.22	this work
<b>5</b>	71.4	99.8		2.50	2.192	[15]

<sup>a</sup> δ = angle between the mean least squares planes (mlsp) of the Cp rings.

<sup>b</sup> ϑ = angle C(Cp)–C(bridging)–C(Cp').

<sup>c</sup> ψ = deviation of the vector of the exocyclic C–C bond by the bridhead C(cp) atom from the mlsp of the corresponding Cp ring.

<sup>d</sup> *d* = mean metal–C(Cp) distance.

<sup>e</sup> *n* = metal–mlsp of the Cp ring distance (normal vector).

also greater for the t.Bu-substituted molecules. The dihedral angle δ between the cp-planes is smaller for non-substituted molecules, and grows with the increase of the bulk of the substituents. The C(cp)–C–C(cp') angle ϑ by the bridge atom does not seem to be influenced. The value of the deviation angle ψ is indicative of the significant intramolecular strain in the –Cl ligand block of the substituted molecules. It is 8 to 10° in **1a**, **2a**, and **2b**, and only 4.8° in **3**.

This value is somewhat greater for the (*syn*) **2b** isomer, compared with the (*anti*) **2a** one, which may suggest that the intramolecular strain is also greater in the (*syn*) isomer. It is noteworthy that the bulk density ρ in solid is 1.41 g cm<sup>-3</sup> for **2a**, and only 1.21 g cm<sup>-3</sup> for **2b**.

So introduction of bulky t.Bu-substituents in the Cp-rings of the Me<sub>2</sub>C-bridged metallocene dichlorides of Ti and Zr does increase intramolecular strain, which is evident from the changes in the geometry of the sandwich moieties of these molecules.

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