

Synthesis and X-ray crystal structures of *ansa*-complexes of titanium, zirconium, and hafnium involving methylene-bis(indenyl) ligand

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Abstract

Synthesis of bis(indenyl)methane and the corresponding *ansa*-complexes of titanium(IV), zirconium(IV), and hafnium(IV) was performed. Mixtures of *rac*- and *meso*-methylene-bis(indenyl)zirconium and -hafnium dichlorides were obtained under a treatment of the respective metal tetrachlorides with bis[3-(tri-*n*-butyltin)indenyl]methane in toluene. The complexes, *rac*-H₂C(indenyl)₂MCl₂, were isolated in 27% (M = Zr) and 31% (M = Hf) yields using a simple work-up process. These zirconium and hafnium complexes were characterized by X-ray crystal structure analysis. Methylene-bis(indenyl)titanium(IV) dichloride was prepared by two different pathways. The first one includes a treatment of TiCl₄(THF)₂ with dilithium salt of bis(indenyl)methane in THF. This procedure gives *rac*-H₂C(indenyl)₂TiCl₂ in 16% only. An alternative reaction involving a treatment of TiCl₄ with bis[3-(tri-*n*-butyltin)indenyl]methane results in *rac*-H₂C(indenyl)₂TiCl₂ with 38% yield. A treatment of *rac*-H₂C(indenyl)₂TiCl₂ with two equivalents of MeLi in diethyl ether gives *rac*-H₂C(indenyl)₂TiMe₂, which has been isolated in 64% yield, and characterized by X-ray crystal structure analysis. © 2001 Published by Elsevier Science B.V. All rights reserved.

Keywords: *ansa*-Metallocenes; Titanium; Zirconium; Hafnium; Tin

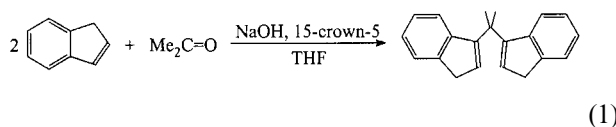
1. Introduction

ansa-Metallocenes involving a CH₂ bridge are scarcely known, since there are no convenient synthetic methods for the respective starting bis-cyclopentadienyl methanes [1–5]. Quite recently, we have found that bis(1-indenyl)methane can be readily prepared under a treatment of indene with paraform or formalin in alcohol media in the presence of a base. Here we describe synthesis and structure investigation of Ti(IV), Zr(IV), and Hf(IV) *ansa*-complexes involving methylene-bis(indenyl) ligand (see our preliminary reports [6] and others [7,8]). This investigation continues our attempts to develop convenient synthetic methods for the simplest *ansa*-metallocenes [9].

2. Results and discussion

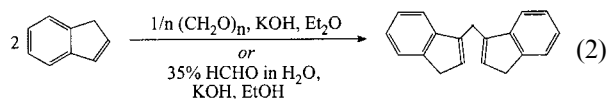
2.1. Synthesis of bis(cyclopentadienyl)methanes

One-pot synthesis of various 2,2'-bis(cyclopentadienyl)propanes is known to include a treatment of the respective cyclopentadienes with acetone in the presence of a base [9,10]. This method is of importance for the preparation of bis-cyclopentadienyl ligands involving two equivalent Cp fragments and a CMe₂ bridge, e.g. [9] (Eq. (1)).

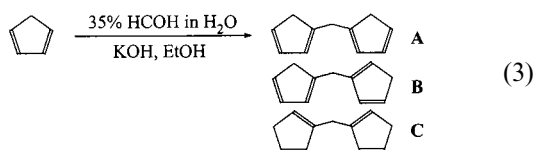


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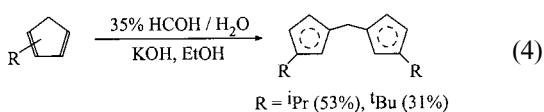
Here we modified this procedure to prepare the desired ligands with a CH₂ bridge. We used paraform (or, alternatively, formalin) instead of an inconvenient and unstable reagent — formaldehyde in THF. We found that the reaction of paraform with freshly distilled indene in the presence of an excess of KOH powder in diethyl ether gives bis(indenyl)methane in 24.5% yield (Eq. (2)). An alternative procedure involving a treatment of indene with formalin and KOH in ethanol resulted in the desired ligand in 64% yield.



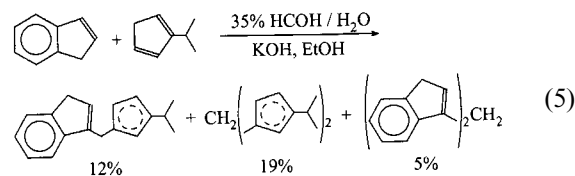
It is of interest that, in similar conditions, an analogous reaction with acetone gives the respective dimethylfulvene, but no 2,2'-bis(1-indenyl)propane. While this paper was prepared, Resconi et al. published an alternative procedure for various bis(indenyl)methanes and even for bis(fluorenyl)methane [8]. The authors used highly basic conditions, such as NaOH or NaOEt in DMF or DMSO. Obviously, these conditions are of importance for the preparation of bis(fluorenyl)methane and bis(indenyl)methanes involving alkyl/aryl fragment in Cp ring. Here, we found that KOH in ethanol can be used as media for this reaction in the case of unsubstituted indene, cyclopentadiene, and substituted cyclopentadienes, such as isopropylcyclopentadiene and *tert*-butylcyclopentadiene. In this manner, mixture of the respective isomeric bis(cyclopentadienyl)methanes (A:B:C = 1:3:2) has been prepared in 27% yield starting from formalin and cyclopentadiene (Eq. (3)).



Analogously, mixtures of isomeric bis(3-alkylcyclopentadienyl)methanes were prepared in a high yield starting from the respective alkylcyclopentadienes and formalin (Eq. (4)).

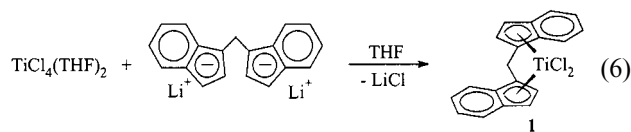


This method can be used for the preparation of unsymmetrical bis(cyclopentadienyl)methanes involving two different cyclopentadienyl fragments with close basicity. On the evidence of NMR spectra, a 50/50 mixture of indene and isopropylcyclopentadiene gives isopropylcyclopentadienyl(indenyl)methane in 12% yield (Eq. (5)).



2.2. Synthesis of *rac*-methylene-bis(indenyl)titanium dichloride and dimethyl complex

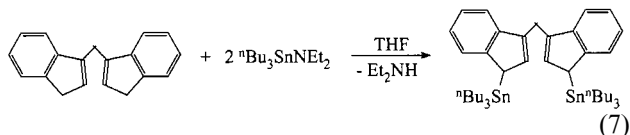
Synthesis of titanium(IV) *ansa*-complexes starting from TiCl₄ and alkali metal or magnesium salts of bridged cyclopentadienes is complicated with a side reduction of Ti(IV) to Ti(III) species. Usually, this results in a low yield of the desired *ansa*-titanocenes. So, synthesis of the desired Ti *ansa*-metallocenes is usually achieved under a treatment of titanium(III) chloride with lithium-cyclopentadienyls and following oxidation of the reaction mixture (e.g. [11,12]). Recently, synthesis and X-ray crystal structure of *rac*-H₂C(4,5,6,7-tetrahydroindenyl)₂TiCl₂ were described [7]. This complex was prepared by the hydrogenation of crude *rac*-H₂C(indenyl)₂TiCl₂, which, unfortunately, has not been isolated in analytically pure form and, therefore, has not been undoubtedly characterized. Here, firstly, we have synthesized *rac*-methylene-bis(indenyl)titanium dichloride (**1**) in an analytically pure form. This compound was prepared in 16% yield under a treatment of TiCl₄(THF)₂ with dilithium salt of bis(indenyl)methane in THF (Eq. (6)). Titanium complex **1** turned out to be completely insoluble in all common solvents, such as ether, THF, CHCl₃, CH₂Cl₂, hydrocarbons, and has been obtained in analytically pure form via continuous washing of the precipitate with CH₂Cl₂ and THF.



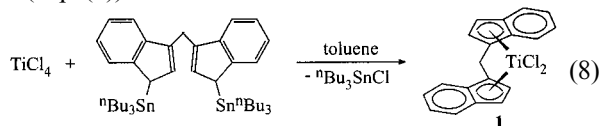
Trialkyltin derivatives of bridged bis-cyclopentadienes were found recently to be more selective reagents compared with the respective alkali metal and magnesium cyclopentadienyl salts [9,13,14]. Here we found that bis[3-(tri-*n*-butyltin)indenyl]methane is a good starting material for the preparation of **1**.

Bis[3-(tri-*n*-butyltin)indenyl]methane has been synthesized in an almost quantitative yield under a treatment of bis(indenyl)methane with two equivalents of ⁿBu₃SnNEt₂ in THF (Eq. (7)). This tin-substituted hydrocarbon was isolated in an analytically pure form after vacuum evaporation of all volatile components of the reaction mixture. Alternative synthetic procedure involves a treatment of dilithium salt of bis(in-

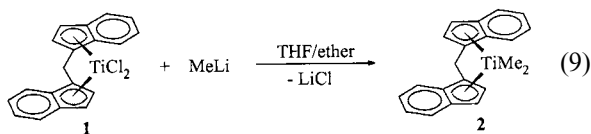
denyl)methane with two equivalents of $n\text{Bu}_3\text{SnCl}$ in diethyl ether.



rac-Methylene-bis(indenyl)titanium dichloride has been prepared in 38% yield under a treatment of TiCl_4 with 2,2'-bis[3-(tri-*n*-butyltin)inden-1-yl]propane in toluene (Eq. (8)).

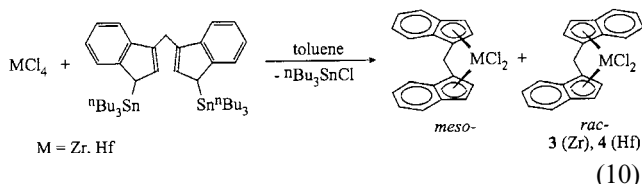


rac-Methylene-bis(indenyl)titanium dimethyl complex **2** has been prepared in 64% yield under a treatment of **1** with two equivalents of MeLi in THF–ether (Eq. (9)).



2.3. Synthesis of zirconium and hafnium ansa-metallocenes involving CH_2 bridge

Complexes of zirconium and hafnium involving chelating methylene-bis(indenyl) ligand have been prepared in a similar manner using transmetalation reaction [9]. Mixtures of *rac*- and *meso*-methylene-bis(indenyl)zirconium and -hafnium dichlorides were prepared under a treatment of ZrCl_4 or HfCl_4 , respectively, with tin derivatives of bis(indenyl)methane (Eq. (10)). The *rac*-complexes were isolated in 27% (Zr, **3**) and 31% (Hf, **4**) yields.



Both synthesis and isolation of **3**, **4**, and well-characterized *rac*-propylidene-bis(indenyl)zirconium dichloride [9] are the same. It should be noted that the complexes involving bis-indenyl ligand with a CH_2 bridge are more soluble in common solvents compared with *rac*-propylidene-bis(indenyl)zirconium dichloride. Recently, Resconi et al. prepared **3** in 9% yield under a treatment of ZrCl_4 with di-potassium salt of bis(indenyl)methane [8]. So, this procedure is a less selective one compared with transmetalation.

2.4. Molecular structures of *rac*- $\text{H}_2\text{C}(\text{indenyl})_2\text{TiMe}_2$ (**2**), *rac*- $\text{H}_2\text{C}(\text{indenyl})_2\text{ZrCl}_2$ (**3**), and *rac*- $\text{H}_2\text{C}(\text{indenyl})_2\text{HfCl}_2$ (**4**)

Figs. 1 and 2 show the structures and numbering schemes for molecules **2**, **3**, and **4**, respectively. Tables 1 and 2 give selected bond lengths and bond angles for these molecules.

Each molecule represents the *rac*-isomer and has the bent sandwich geometry, with two σ -ligands (CH_3 ligands in **2** and Cl ligands in **3** and **4**) in the bisecting plane. The angle between the σ -bonds differs essentially in **2** $94.0(2)^\circ$ compared to that in **3** $99.21(5)^\circ$ and **4** $98.15(6)^\circ$, in which these values are almost equal to one another. The dihedral angle between the planar η^5 -Cp fragments of the indenyl ligands is equal to 111.9° in **2**, 107.7° in **3**, and 108.8° in **4**, whereas the angle centroid–Cp(1)–M–centroid–Cp(2) is equal to 121.6° , 117.2° , and 118.0° , respectively. The rest of the most important geometrical parameters of the bent sandwich

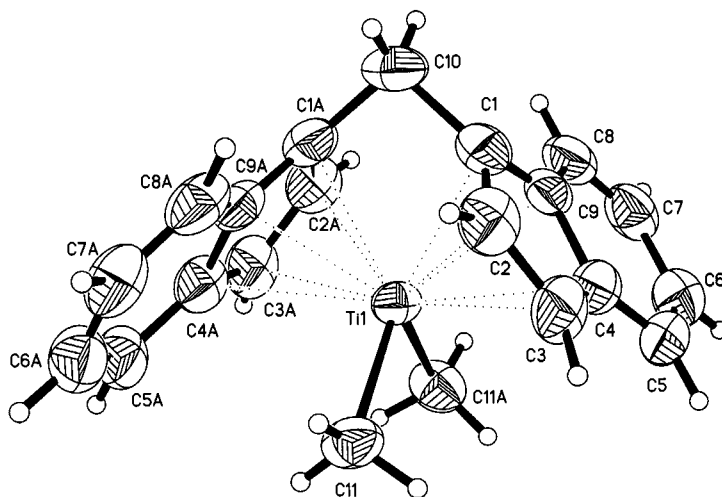


Fig. 1. View of *rac*- $\text{H}_2\text{C}[\text{indenyl}]_2\text{TiMe}_2$ (**2**).

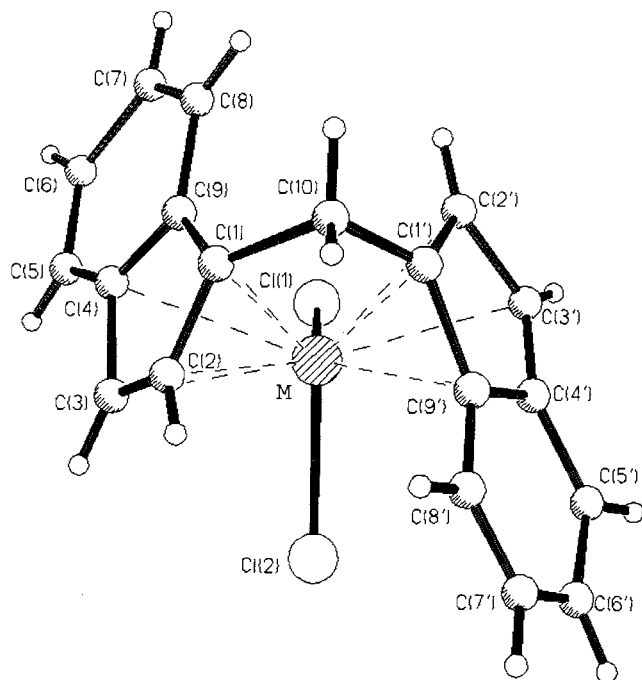


Fig. 2. View of *rac*-H₂C[indenyl]₂MCl₂, where M = Zr (3), Hf (4).

Table 1
Selected bond length (Å) in **2**, **3**, and **4**^a

Bond	2 (M = Ti)	3 (M = Zr)	4 (M = Hf)
M(1)–Cl(1)	–	2.411(1)	2.3844(12)
M(1)–C(1)	2.344(4)	2.428(3)	2.422(4)
M(1)–C(2)	2.357(4)	2.457(3)	2.428(5)
M(1)–C(3)	2.462(4)	2.556(3)	2.526(5)
M(1)–C(4)	2.544(4)	2.618(3)	2.601(5)
M(1)–C(9)	2.441(3)	2.515(3)	2.493(4)
M(1)–C(11)	2.122(4)	–	–
C(1)–C(2)	1.417(6)	1.412(5)	1.424(7)
C(1)–C(9)	1.422(6)	1.426(5)	1.421(7)
C(1)–C(10)	1.520(5)	1.510(5)	1.505(7)
C(2)–C(3)	1.407(6)	1.402(6)	1.381(8)
C(3)–C(4)	1.419(7)	1.414(5)	1.408(8)
C(4)–C(5)	1.416(7)	1.405(6)	1.410(8)
C(4)–C(9)	1.434(5)	1.452(4)	1.430(6)
C(5)–C(6)	1.356(7)	1.354(5)	1.366(8)
C(6)–C(7)	1.411(7)	1.415(6)	1.416(9)
C(7)–C(8)	1.354(7)	1.342(6)	1.352(8)
C(8)–C(9)	1.425(6)	1.411(5)	1.434(6)

^a Symmetry transformations used to generate equivalent atoms: # 1 $-x+1, y, -z+3/2$.

differ insignificantly in **2** compared to that in **3** and **4**. For instance, the C(1)–C(10) bond between the Cp ring and the bridging carbon atom is inclined to the plane of the Cp ring by 15.9 in **2**, 14.4 in **3**, and 15.2 in **4**. Such a geometrical distortion corresponds to a displacement of the bridging carbon atom from the Cp-ring plane by 0.413, 0.376, and 0.390 Å in **2**, **3**, and **4**, respectively. The CCC bond angle at the bridging carbon atom vary little in these molecules (100.0(4)°, 101.3(4)°, and

101.8(6)°). The distance M–C(1) with the carbon atom involved in the bridging CCC system is the shortest one, and the distance M–C(4) is the longest one.

3. Experimental

All manipulations have been done either on the high-vacuum line in an all-glass apparatus equipped with polytetrafluoroethylene stopcocks or in an atmosphere of thoroughly purified argon using the standard Schlenk technique. THF was distilled over LiAlH₄. Toluene was distilled over Na/K alloy and kept over CaH₂. CH₂Cl₂, as well CDCl₃ and CD₂Cl₂ were distilled over P₄O₁₀ and kept over 3 Å molecular sieves. ⁿBu₃SnNEt₂ was prepared according to the published procedure [15]. ¹H-NMR spectra were recorded with a Bruker AM 360 spectrometer.

3.1. Bis(1-indenyl)methane

3.1.1. Method I

A mixture of 104.56 g (0.90 mol) of freshly distilled indene and 137.90 g of KOH powder in 300 ml of diethyl ether was stirred for 1 h in argon at room temperature (r.t.). Then, 14.00 g (0.47 mol) of paraform was added, and the crimson suspension was stirred overnight. The resulting suspension was mixed with ca. 500 cm³ of ice. Then, this mixture was neutralized with 10% HCl, the organic layer was separated, and an aqueous one was washed with 2 × 100 ml of ether. Combined organic fractions were dried over K₂CO₃. Ether was removed under reduced pressure. Fractional

Table 2
Selected bond angles in **2**, **3**, and **4**^a

Angle	2 (M = Ti)	3 (M = Zr)	4 (M = Hf)
Cl(1)–M(1)–Cl(1) # 1	–	99.21(5)	98.15(6)
C(11) # 1–M(1)–C(11)	94.0(2)	–	–
C(2)–C(1)–C(9)	107.4(4)	107.6(3)	105.9(4)
C(2)–C(1)–C(10)	123.5(4)	124.3(3)	123.9(4)
C(9)–C(1)–C(10)	125.8(3)	125.5(3)	126.9(4)
C(1)–C(2)–C(3)	108.7(4)	109.2(4)	109.5(5)
C(2)–C(3)–C(4)	108.7(4)	108.7(3)	109.2(5)
C(3)–C(4)–C(5)	132.7(4)	133.2(3)	133.3(5)
C(3)–C(4)–C(9)	106.9(4)	107.0(3)	106.5(5)
C(5)–C(4)–C(9)	120.3(4)	119.8(4)	120.1(5)
C(4)–C(5)–C(6)	119.0(4)	119.2(4)	119.1(5)
C(5)–C(6)–C(7)	120.9(5)	121.2(4)	121.0(5)
C(6)–C(7)–C(8)	122.2(4)	121.3(4)	121.8(5)
C(7)–C(8)–C(9)	119.1(4)	120.3(4)	119.0(5)
C(1)–C(9)–C(8)	133.3(4)	134.5(3)	132.2(5)
C(1)–C(9)–C(4)	108.3(4)	107.5(3)	108.8(4)
C(4)–C(9)–C(8)	118.4(4)	118.1(4)	119.0(5)
C(1) # 1–C(10)–C(1)	100.0(4)	101.3(4)	101.8(6)

^a Symmetry transformations used to generate equivalent atoms: # 1 $-x+1, y, -z+3/2$.

distillation gave bis(1-indenyl)methane as a pale-yellow oil, b.p. 178°C/0.2 mm Hg. Yield 26.91 g (24.5%). Anal. Calc. for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.57; H, 6.64%. $^1\text{H-NMR}$ (CDCl_3): δ 7.3–7.8 (m, 8H, C_6H_4), 6.4 (m, 2H, 2-H), 4.1 (m, 2H, CH_2), 3.5 (s, 4H, 1-H).

3.1.2. Method II

A mixture of 40.0 g (0.34 mol) of freshly distilled indene and 56.7 g of KOH powder in 200 ml of ethanol was stirred in argon at r.t. for 4 h. Then 13.3 ml of 35% formalin was added dropwise for 1 h. This mixture was stirred at ambient temperature for 1 day. The resulting mixture was treated with ca. 100 cm^3 of ice, then neutralized with 2 M HCl, and washed with 300 ml of ether. The organic fraction was diluted with 3×300 ml of cold water and dried over K_2CO_3 . Ether was removed under reduced pressure. Fractional distillation gave bis(1-indenyl)methane as a pale-yellow oil, b.p. 166–168°C/0.1 mm Hg. Yield 26.9 g (64%). Anal. Found: C, 93.51; H, 6.70%.

3.2. Bis[3-(tri-*n*-butyltin)inden-1-yl]methane

A total of 23.74 g (65.6 mmol) of $^n\text{Bu}_3\text{SnNEt}_2$ was added dropwise for 0.5 h to a stirred solution of 8.01 g (32.78 mmol) of bis(1-indenyl)methane in 35 ml of THF at -50°C . Then, this mixture was warmed to r.t. for 2 h and stirred overnight. The solution was concentrated under reduced pressure, and the resulting oil was dried in vacuo to remove THF traces. This procedure yielded an analytically pure mixture of isomeric products in an almost quantitative yield. Anal. Calc. for $C_{43}H_{68}\text{Sn}_2$: C, 62.80; H, 8.33. Found: C, 63.11; H, 8.50%.

3.3. *rac*-Methylene-bis(indenyl)zirconium dichloride

A solution of 26.96 g (32.78 mmol) of bis[3-(tri-*n*-butyltin)inden-1-yl]methane in 30 ml of toluene was added dropwise for 2 h to a suspension of 7.64 g (32.78 mmol) of ZrCl_4 in 100 ml of toluene. The mixture was stirred for 4 h at 100°C and then cooled to 0°C . Orange–red crystalline solid was filtered off, washed with 5×40 ml of CH_2Cl_2 , 25 ml of THF, and dried in vacuo. This procedure yielded 3.58 g (27%) of the title compound. Anal. Calc. for $C_{19}H_{14}Cl_2\text{Zr}$: C, 56.43; H, 3.49. Found: C, 56.61; H, 3.55%. $^1\text{H-NMR}$ (CDCl_3): δ 7.0–7.6 (m, 8H, C_6H_4), 6.45 (d, $J_{\text{HH}}^3 = 3.6$ Hz, 2H, 3-H), 5.95 (d, 2H, 2-H), 4.8 (s, 2H, CH_2).

3.4. *rac*-Methylene-bis(indenyl)hafnium dichloride

Following the procedure described for *rac*-methylene-bis(indenyl)zirconium dichloride, 27.81 g (33.81

mmol) of bis[3-(tri-*n*-butyltin)inden-1-yl]methane and 10.47 g (32.69 mmol) of HfCl_4 in 150 ml of toluene gave 4.98 g (31%) of orange crystals of the title compound. Anal. Calc. for $C_{19}H_{14}Cl_2\text{Hf}$: C, 46.41; H, 2.87. Found: C, 46.53; H, 2.75%. $^1\text{H-NMR}$ (CD_2Cl_2): δ 7.0–7.6 (m, 8H, C_6H_4), 6.41 (d, $J_{\text{HH}}^3 = 3.23$ Hz, 2H, 3-H), 5.86 (d, 2H, 2-H), 4.76 (s, 2H, CH_2).

3.5. *rac*-Methylene-bis(indenyl)titanium(IV) dichloride

3.5.1. Method I

A solution of 7.85 g (26.0 mmol) of $\text{TiCl}_4 \cdot 2\text{THF}$ in 50 ml of THF was added at 0°C to a solution of 6.66 g (26.0 mmol) of dilithium salt of bis(1-indenyl)methane in 50 ml of THF. This mixture was stirred overnight. Then, a stream of HCl was passed through the resulting solution for 1 h. The solvent was removed under reduced pressure, and a solid residue was dried in vacuo. A greenish–brown crystalline solid was washed consistently with 10 ml of 4 M HCl, 10 ml of H_2O , 15 ml EtOH, 2×15 ml of Et_2O , and was then dried in vacuo. Yield 1.50 g (16%) of the title compound. Anal. Calc. for $C_{19}H_{14}Cl_2\text{Ti}$: C, 63.20; H, 3.91. Found: C, 63.33; H, 3.99%. $^1\text{H-NMR}$ (CDCl_3): δ 7.0–7.6 (m, 8H, C_6H_4), 6.85 (d, $J_{\text{HH}}^3 = 3.36$ Hz, 2H, 3-H), 5.44 (d, 2H, 2-H), 4.89 (s, 2H, CH_2).

3.5.2. Method II

A solution of 24.20 g (29.42 mmol) of bis[3-(tri-*n*-butyltin)inden-1-yl]methane in 30 ml of toluene was added dropwise for 1.5 h to a solution of 3.23 ml (5.58 g, 29.42 mmol) of TiCl_4 in 90 ml of toluene. This mixture was stirred for 3 h at 90°C and then cooled to 0°C . Greenish–brown crystals were filtered off, washed with 50 ml of toluene, 2×25 ml of hexane, and 4×25 ml of CH_2Cl_2 ; it was then dried in vacuo. This procedure yielded 4.03 g (38%) of the title compound. Anal. Found: C, 63.33; H, 3.99%.

3.6. *rac*-Methylene-bis(indenyl)titanium(IV) dimethyl complex

To a suspension of 3.96 g (10.97 mmol) of *rac*-methylene-bis(indenyl)titanium(IV) dichloride in 100 ml of THF, 12 ml (23.59 mmol) of 1.95 M MeLi in ether was added dropwise for 0.6 h. This mixture was stirred for 0.5 h. During this time the precipitate dissolved. The resulting claret solution was evaporated to dryness. Crystallization from pentane gave the title compound as a dark-green crystalline solid. Yield 2.25 g (64%). Anal. Calc. for $C_{21}H_{20}\text{Ti}$: C, 78.76; H, 6.29. Found: C, 78.90; H, 6.38%. $^1\text{H-NMR}$ (C_6D_6): δ 6.85–7.63 (m, 8H, C_6H_4), 6.80 (d, $^3J_{\text{HH}} = 3.22$ Hz, 2H, 3-H), 4.98 (d, 2H, 2-H), 3.58 (s, 2H, CH_2), -0.48 (s, 6H, Ti-CH_3).

Table 3

Crystal data, data collection, structure solution and refinement parameters for **2**, **3** and **4**

Compound	2	3	4
Empirical formula	C ₂₁ H ₂₀ Ti	C ₁₉ H ₁₄ Cl ₂ Zr	C ₁₉ H ₁₄ Cl ₂ Hf
Formula weight	320.27	404.42	983.38
Colour, habit	Dark green, block	Yellow, block	Yellow, prism
Crystal size (mm)	0.56 × 0.52 × 0.46	0.42 × 0.24 × 0.36	0.28 × 0.16 × 0.12
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	C2/c
Unit cell dimensions			
<i>a</i> (Å)	15.845(3)	16.100(3)	16.047(3)
<i>b</i> (Å)	9.747(2)	9.941(2)	9.904(2)
<i>c</i> (Å)	11.897(2)	11.581(2)	11.598(3)
β (°)	120.78(3)	121.48(3)	121.52(3)
Volume (Å ³)	1578.5(5)	1580.7(5)	1571.3(6)
<i>Z</i>	4	4	4
<i>D</i> _{calc} (g·cm ⁻³)	1.348	1.699	2.078
Absorption coefficient (mm ⁻¹)	4.511	1.026	6.971
<i>F</i> (000)	672	808	936
Diffractometer	Rigaku AFC-6S	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4
Temperature (K)	293	293	293
Radiation (λ, Å)	Graphite-monochromatized Cu-K _α (1.54184)	Graphite-monochromatized Mo-K _α (0.71073)	Graphite-monochromatized Mo-K _α (0.71073)
Scan mode	<i>ω</i>	<i>ω</i> /2 <i>θ</i>	<i>ω</i>
Scan width (°)	1.5 + 0.15 tan <i>θ</i>	0.8 + 0.35 tan <i>θ</i>	0.8 + 0.35 tan <i>θ</i>
Min/max scan speed	8/8	4/8	4/8
<i>θ</i> Range (°)	5.58–74.95	2.53–27.49	2.54–28.50
Index ranges	−1 ≤ <i>h</i> ≤ 18, −1 ≤ <i>k</i> ≤ 12, 14 ≤ <i>l</i> ≤ 13	−11 ≤ <i>h</i> ≤ 19, −13 ≤ <i>k</i> ≤ 0, 0 ≤ <i>l</i> ≤ 16	−22 ≤ <i>h</i> ≤ 22, 0 ≤ <i>k</i> ≤ 16, −18 ≤ <i>l</i> ≤ 19
Reflections collected	1857	1352	2269
Independent reflections	1476 [<i>R</i> _{int} = 0.0317]	1292 [<i>R</i> _{int} = 0.0509]	1798 [<i>R</i> _{int} = 0.0453]
Absorption correction	Empirical (ψ-scan)	None	Empirical (ψ-scan)
Min/max transmission	0.96543/0.61245		0.8564/0.6483
Solution method	Direct methods (SHELX-86)		
Refinement method	Full-matrix least-squares on <i>F</i> ² (SHELXL-93)		
Data/restraints/parameters	1470/0/103	1292/0/102	1787/0/102
Weighting scheme <i>w</i> ⁻¹	σ ² (<i>F</i> ²) + (0.0971 <i>P</i>) ² + 2.71 <i>P</i> where <i>P</i> = (2 <i>F</i> _c ² + <i>F</i> _o ²)/3	σ ² (<i>F</i> ²) + (0.0507) ² + 0.0 <i>P</i>	σ ² (<i>F</i> ²) + (0.0417 <i>P</i>) ² + 0.0 <i>P</i>
Goodness-of-fit on <i>F</i> ²	1.190	1.040	1.068
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0523, <i>wR</i> ₂ = 0.1575	<i>R</i> ₁ = 0.0286, <i>wR</i> ₂ = 0.0736	<i>R</i> ₁ = 0.0242, <i>wR</i> ₂ = 0.0593
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0640, <i>wR</i> ₂ = 0.1965	<i>R</i> ₁ = 0.0372, <i>wR</i> ₂ = 0.0762	<i>R</i> ₁ = 0.0306, <i>wR</i> ₂ = 0.0629
Largest difference peak/hole (e·Å ⁻³)	0.390/−0.409	0.619/−0.388	1.442/−0.981

3.7. X-ray diffraction study of **2**, **3** and **4**

Details of the X-ray experiments are given in Table 3.

The experimental data were measured on an Rigaku AFC-6S diffractometer for **2** and on an Enraf-Nonius CAD4 diffractometer for **3** and **4** using graphite-monochromatized Cu-K_α radiation and Mo-K_α radiation, respectively. Experimental reflections were corrected for Lorentz and polarization. Empirical absorption correction was applied for **2** and **3**. The molecular structure of **3** has been recently established by others [8]. The two determinations are in agreement within the experimental error.

The structures were solved by direct methods. Least squares refined on *F*² was performed anisotropically for

non-hydrogen atoms in a full-matrix approximation. The hydrogen atoms were calculated geometrically (*d*(C–H) = 0.94 Å) and included in the refinement using a riding model with *B*_{iso} equal to 1.5*B*_{eq} of the parent carbon atom. All of the structures were solved and refined using the SHELXS-86 [16] and SHELXL-93 [17] software.

4. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 145725 for compound **2**, 145726 for compound **3**, and 145724 for compound **4**. Copies of this information may be ob-

tained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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