

Synthesis and molecular structure of *rac*-methylenebis(4,5,6,7-tetrahydro-1-indenyl) titanium dichloride

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Abstract

The reaction of indenylpotassium with 0.5 equiv. of chloromethylpivalate yields bis(3-indenyl)methane (1). Double deprotonation of 1 with two equiv of BuLi, reaction with TiCl₄ · 2THF and subsequent hydrogenation yields *rac*-methylenebis(4,5,6,7-tetrahydro-1-indenyl) titanium dichloride (3) in 16% overall yield. The molecular structure of (3) reveals a very small acute angle of 98.9(2)° at the methylene bridge carbon atom. © 1997 Elsevier Science S.A.

Keywords: Indene; Fluorene; Titanium; *ansa*-Metallocene

1. Introduction

In recent years, an impressive number of group IV *ansa*-metallocenes have been employed as homogeneous catalysts for polymerization of α -olefins. Especially, chiral C₂-symmetric ethylene bridged bis(indenyl) complexes have received considerable interest in isospecific polymerization of propene (for review, see [1]) and asymmetric organic synthesis (for review, see [2]).

Preparation of symmetric methylene bridged *ansa*-metallocenes has, however, received much less attention, in part due to the difficult synthesis of the corresponding methylene bridged ligands. To our knowledge, the only example of a methylene bridged group IV bis(indenyl) complex is methylenebis(1-indenyl)hafnium dichloride reported by Ewen and co-workers [3]. They prepared bis(1-indenyl)methane by reacting indenyl-lithium with CH₂I₂ at –78°C. Characterization of the product was incomplete and the yield not reported.

We present here a simple high yield approach to methylene bridged ligands using chloromethylpivalate

and the potassium salt of the cyclopentadienyl moiety ¹. In addition, the molecular structure of the first crystallographically characterized methylene bridged bis(tetrahydroindenyl) *ansa*-metallocene, *rac*-methylenebis(4,5,6,7-tetrahydro-1-indenyl)titanium dichloride, is reported.

2. Results and discussion

Bis(3-indenyl)methane (1) was synthesized in 70% yield by reacting indenylpotassium with chloromethylpivalate in THF (Scheme 1). Bis(9-fluorenyl)methane (4) and (3-indenyl)(9-fluorenyl)methane (5) were prepared by a similar procedure (see Section 3).

Double deprotonation of 1 with BuLi and the subsequent reaction with TiCl₄ · 2THF gave after workup and washings methylenebis(indenyl)titanium dichloride (2) in 64% yield ². The crude product was suspended in

¹ A similar approach, by reacting cyclopentadienylsodium with chloromethylacetate was employed in the synthesis of bis(cyclopentadienyl)methane; see ref. [4].

² Due to the poor solubility of 2, it was not possible to determine the purity by NMR.

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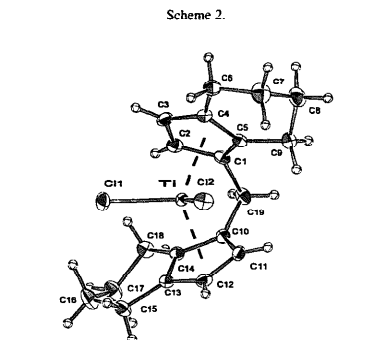
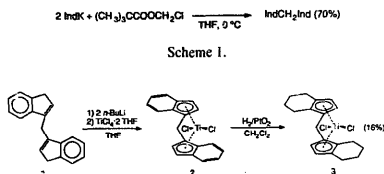


Fig. 1. Molecular structure of (*S,S*) **3** (ORTEP view, ellipsoids at 30% probability level).

CH₂Cl₂ and hydrogenated in the presence of PtO₂ to yield, after crystallization from toluene, *rac*-methylenebis(4,5,6,7-tetrahydro-1-indenyl)titanium dichloride (**3**) in 16% overall yield (Scheme 2).

The ¹H-NMR spectrum of **3** shows the characteristic doublets from H_α and H_β at 5.55 and 6.57 ppm, values close to those observed for the ethylene (5.55 and 6.58 ppm) [5], propylene (5.62 and 6.00 ppm) [6], and butylene (5.49 and 6.10 ppm) [7] bridged bis(4,5,6,7-tetrahydro-1-indenyl) titanium dichlorides.

The molecular structure of **3** was determined by

Table 1
Selected intramolecular distances (Å) and angles (°) for (**3**)

Ti–Cl(1)	2.337(1)	Ti–Ce(1) ^a	2.077	C(1)–C(19)	1.508(3)
Ti–Cl(2)	2.336(1)	Ti–Ce(2) ^a	2.078	C(10)–C(19)	1.506(4)
Ti–C(1)	2.336(2)	Ti–C(10)	2.338(2)	C(1)–C(10)	2.299(4)
Ti–C(2)	2.284(2)	Ti–C(11)	2.302(2)	Cp(1)–Cp(2) ^b	67.21
Ti–C(3)	2.413(2)	Ti–C(12)	2.413(2)	C(1)–Ti–C(12)	96.70(4)
Ti–C(4)	2.520(2)	Ti–C(13)	2.506(2)	C(1)–C(19)–C(10)	98.9(2)
Ti–C(5)	2.441(2)	Ti–C(14)	2.430(2)	Ce(1)–Ti–Ce(2)	121.0
C(1)–C(2)	1.418(3)	C(1)–C(5)	1.413(3)	C(13)–C(14)	1.423(3)
C(2)–C(3)	1.417(4)	C(10)–C(11)	1.408(3)	C(10)–C(14)	1.427(3)
C(3)–C(4)	1.394(3)	C(11)–C(12)	1.406(4)		
C(4)–C(5)	1.423(3)	C(12)–C(13)	1.396(3)		

^a Ce(1) and Ce(2) denote the centroids of the five-membered portions of the indene rings, with the lowest and highest crystallographic numbering, respectively.

^b Angle between the cyclopentadienyl planes.

Table 2
Positional and equivalent isotropic thermal parameters (Å²) for (**3**)^a

Atom	x	y	z	B _{eq} ^b / B
Ti	1.00324(4)	0.26018(3)	0.85786(3)	1.80(2)
Cl(1)	1.16054(8)	0.22070(5)	0.72227(5)	3.81(3)
Cl(2)	0.77875(7)	0.19985(5)	0.78417(5)	3.22(3)
C(1)	1.0083(3)	0.3956(2)	0.9581(2)	2.3(1)
C(2)	1.1136(3)	0.4033(2)	0.8777(2)	2.6(1)
C(3)	1.0313(3)	0.4127(2)	0.7826(2)	2.7(1)
C(4)	0.8766(3)	0.4102(2)	0.8025(2)	2.3(1)
C(5)	0.8617(3)	0.3975(2)	0.9108(2)	2.2(1)
C(6)	0.7431(3)	0.4258(2)	0.7293(2)	3.2(1)
C(7)	0.5952(3)	0.4164(3)	0.7816(2)	4.2(1)
C(8)	0.5952(3)	0.4519(2)	0.8913(2)	3.8(1)
C(9)	0.7092(3)	0.3980(2)	0.9600(2)	2.8(1)
C(10)	1.0638(3)	0.2554(2)	1.0349(2)	2.2(1)
C(11)	0.9404(3)	0.1953(2)	1.0136(2)	2.5(1)
C(12)	0.9922(3)	0.1184(2)	0.9576(2)	2.5(1)
C(13)	1.1477(3)	0.129(2)	0.9428(2)	2.2(1)
C(14)	1.1934(3)	0.2153(2)	0.9884(2)	2.1(1)
C(15)	1.2576(3)	0.0628(2)	0.8957(2)	3.0(1)
C(16)	1.4191(3)	0.1028(2)	0.8921(3)	4.1(1)
C(17)	1.4608(3)	0.1625(2)	0.9832(3)	3.8(1)
C(18)	1.3563(3)	0.2463(2)	0.9938(2)	2.8(1)
C(19)	1.0483(3)	0.3565(2)	1.0636(2)	2.8(1)

^a Estimated standard deviations are given in parentheses.

^b B_{eq} is defined as (8π²/3)Σ_iU_ia_i²/a_i.

X-ray diffraction (Fig. 1, Table 1, Table 2). Complex **3** shows the expected geometry, with planar C₅-rings, the average deviations from planarity being less than 0.01 Å. The C–C bond distances in the C₅-rings, ranging from 1.394(3) Å to 1.427(3) Å, are within the range normally observed for crystallographically determined structures of *ansa*-bis(tetrahydroindeno)l)titanium dichlorides [5,6,8,9]. However, the Ti–C bond lengths (*vide infra*) are no longer equal and are considerably shortened towards the bridgehead and C_α carbon atoms. The bonding requirements at the methylene bridge, as well as those at the titanium center, force the metal atom out from the ligand framework, similar to methylenebis(cyclopentadienyl)titanium dichloride [10]. A very small acute angle of 98.9(2)° at the methylene

bridge carbon atom brings the bridgehead atoms into a close contact of 2.299(4) Å. The small Cp–Ti–Cp angle of 121° gives rise to an enlarged Cl–Ti–Cl angle of 96.70(4)°. Similar observations have been made for symmetrical [10,11] and unsymmetrical [12] one carbon bridged *ansa*-metallocenes. Attempts to prepare the zirconium analogue of **2** via a salt metathesis reaction of 1–Li₂ or 1–K₂ with ZrCl₄ under various reaction conditions were unsuccessful.

3. Experimental section

Reactions with organometallic compounds were carried out under argon in Schlenk-type glassware. Solvents were dried and distilled under argon prior to use. Fluorene, titanium tetrachloride and chloromethylpivalate (Aldrich) were used without further purification. Indene (Aldrich) was distilled and potassium hydride (Fluka) washed copiously with hexane prior to use. NMR spectra were recorded with a JEOL GX 400 (¹H, 400 MHz; ¹³C, 100.6 MHz) NMR spectrometer with Me₄Si as internal standard. Direct inlet ionization mass spectra (EIMS) were obtained at 70 eV with a VG-7070E mass spectrometer. Melting points are uncorrected.

3.1. Bis(3-indenyl)methane (1)

To a suspension of KH (23.8 g, 593 mmol) in THF (1000 ml) was added dropwise a solution of indene (69.0 g, 594 mmol) in THF (100 ml) at room temperature. The reaction mixture was stirred at 60°C for 3 h, upon which hydrogen evolution stopped. The solution was cooled to 0°C and treated dropwise with chloromethylpivalate (45.2 g, 300 mmol) in THF (100 ml) and stirred at room temperature for 16 h. The resulting suspension was poured into water and the organic phase was evaporated. The residue was taken up in Et₂O (500 ml) and washed with water (200 ml), 5% HCl (200 ml), and water (200 ml), respectively. The organic phase was dried over Na₂SO₄ and evaporated. The resulting dark brown oil was fractionated to give bis(3-indenyl)methane (51.3 g, 210 mmol, 70%) as a pale yellow oil (b.p. 141–143°C, 0.05 mmHg). The product can be crystallized from ethanol to give white needles (m.p. 60–61°C). ¹H-NMR (CDCl₃) 1: δ 7.43 (d, ³J = 7.0 Hz, 2H), 7.36 (d, ³J = 7.3 Hz, 2H), 7.25 (t, ³J = 7.3 Hz, 2H), 7.17 (t, ³J = 7.0 Hz, 2H), 6.20 (s, 2H), 3.80 (d, ²J = 1.5 Hz, 2H), 3.30 (s, 4H). ¹³C-NMR (CDCl₃) 1: δ 145.3, 144.5, 141.6, 130.1, 126.1, 124.6, 123.8, 119.4, 37.8, 26.8. EIMS (calculated/found): 244.1258/244.1258.

3.2. Methylenebis(1-indenyl)titanium dichloride (2)

A solution of **1** (9.17 g, 37.5 mmol) in THF (200 ml) was cooled to –80°C and BuLi (33 ml of 2.5 M

solution in hexanes, 82.5 mmol) added dropwise. A yellow suspension formed. The dianion dissolved upon warming to room temperature to give a deep red solution. In a separate vessel TiCl₄ · 2 THF was dissolved in THF (250 ml). Both solutions were added simultaneously to vigorously stirred THF (100 ml) over 2 h. HCl was bubbled through the dark brown suspension for 30 sec. The solvents were evaporated and the residue taken up in Et₂O (200 ml), filtered and washed copiously with Et₂O until the filtrate was nearly colorless. The solid was washed with 2 M HCl (10 ml), water (10 ml), ethanol (2 × 10 ml) and taken up in Et₂O. Filtration yielded a brown powder which was dried *in vacuo* to give **2** (8.80 g, 24.1 mmol, 64%). The mass spectrum of **2** showed parent ions of composition C₁₉H₁₄TiCl₂⁺ at *m/e* = 366–358 in the appropriate isotope ratios. The base peak, however, corresponded to C₁₉H₁₃TiCl⁺ (M⁺–HCl) at *m/e* = 328–322.

3.3. Methylenebis(4,5,6,7-tetrahydro-1-indenyl)titanium dichloride (3)

A suspension of **2** (8.1 g, 24.1 mmol) and PtO₂ (300 mg) in CH₂Cl₂ (150 ml) was kept under hydrogen at 70 bar for 14 h. The deep red suspension was diluted with additional CH₂Cl₂ (150 ml), filtered through Celite and evaporated. Crystallization of the residue from toluene yielded **3** (2.2 g, 6.0 mmol, 16% overall yield) as dark red crystals.

¹H-NMR (CDCl₃) **3**: δ 6.57 (d, ³J = 2.9 Hz, 2H), 5.55 (d, ³J = 2.9 Hz, 2H), 4.00 (s, 2H), 3.08 (dt, ³J = 17.1, 6.9 Hz, 2H), 2.71 (dt, ³J = 17.2, 6.0 Hz, 2H), 2.53 (m, 2H), 2.11 (dt, ³J = 16.6, 5.9 Hz, 2H), 1.93 (m, 2H), 1.68 (m, 2H), 1.53 (m, 4H). ¹³C-NMR (CDCl₃) **3**: δ 141.6, 125.4, 124.9, 112.6, 98.8, 24.9, 24.7, 24.2, 21.8, 21.7. The mass spectrum of **3** showed parent ions of composition C₁₉H₂₂TiCl₂⁺ at *m/e* = 374–366 in the appropriate isotope ratios. The base peak, however, corresponded to C₁₉H₂₀Ti⁺ (M⁺–2HCl) at *m/e* = 298–294.

3.4. Bis(9-fluorenyl)methane (4)

To a suspension of KH (2.21 g, 55 mmol) in THF (100 ml) was added dropwise a solution of fluorene (9.14 g, 55 mmol) in THF (50 ml). The reaction mixture was stirred for 14 h at ambient temperature and treated dropwise with a solution of chloromethylpivalate (4.06 g, 27 mmol) in THF (20 ml) at 0°C. After 16 h the mixture was poured into water and the organic phase dried over Na₂SO₄. The white residue was washed with Et₂O (3 × 50 ml) to yield bis(9-fluorenyl)methane (7.63 g, 22 mmol, 81%). ¹H-NMR (CDCl₃) **4**: δ 7.82 (d, ³J = 7.6 Hz, 4H), 7.55 (dd, ³J = 7.5 Hz, ⁴J = 0.7 Hz, 4H), 7.40 (t, ³J = 7.4 Hz, 4H), 7.28 (dt, ³J = 7.5 Hz, ⁴J = 1.2 Hz, 4H), 4.41 (t, ³J = 7.5 Hz, 2H), 2.23 (t, ³J = 7.6 Hz, 2H). ¹³C-NMR (CDCl₃) **4**: δ 147.42.

140.92, 127.23, 126.95, 124.98, 120.05, 45.81, 33.79. EIMS (calculated/found): 344.1565/344.1565.

3.5. (3-Indenyl)(9-fluorenyl)methane (5)

To a suspension of K^{H} (1.29 g, 32 mmol) in THF (60 ml) was added dropwise a solution of indene (1.86 g, 16 mmol) and fluorene (2.66 g, 16 mmol) in THF (50 ml). The reaction mixture was stirred for 14 h at ambient temperature and treated dropwise with a solution of chloromethylpivalate (2.41 g, 16 mmol) in THF (20 ml) at 0°C . After 16 h the mixture was poured into water and the organic phase dried over Na_2SO_4 . The residue was extracted with Et_2O (3×50 ml). The combined extracts were evaporated and the residue extracted with diisopropylether (100 ml). Filtration through a short path of Celite, concentration and cooling to -15°C yielded (3-indenyl)(9-fluorenyl)methane (1.76 g, 6.0 mmol, 37%) as a white powder. $^1\text{H-NMR}$ (CDCl_3) δ : 7.77 (dt, $^3J = 7.6$ Hz, $^4J = 0.8$ Hz, 2H), 7.54–7.51 (m, 2H), 7.44 (dq, $^3J = 7.5$ Hz, $^4J = 0.8$ Hz, 2H), 7.38–7.31 (ca, 3H), 7.27–7.22 (m, 3H), 6.27 (t, $^4J = 1.2$ Hz, 1H), 4.37 (t, $^3J = 7.1$ Hz, 1H), 3.43 (d, $^4J = 1.8$ Hz, 2H), 3.07 (dq, $^3J = 7.3$ Hz, $^4J = 1.5$ Hz, 2H). $^{13}\text{C-NMR}$ (CDCl_3) δ : 147.35, 145.20, 144.53, 142.30, 140.77, 130.29, 127.11, 126.77, 126.12, 124.78, 123.93, 119.85, 119.79, 119.11, 45.44, 37.82, 32.34. EIMS (calculated/found): 294.1408/294.1408.

3.6. Molecular structure determination

Cell parameters and X-ray diffraction intensities were determined on a Rigaku AFC5S diffractometer at 296 K ($\text{Mo-K}\alpha$, $\lambda = 0.71069$ Å), graphite monochromator, ω - 2θ scan, $4.0^{\circ}/\text{min}$ (in omega), $2\theta_{\text{max}} = 50.0^{\circ}$, 3018 unique reflections. The crystals of **3** are monoclinic, space group $\text{P}2_1/n$ ($\#14$); $a = 8.804(3)$ Å, $b = 14.359(2)$ Å, $c = 12.938(2)$ Å, $b = 91.69(2)^{\circ}$, $Z = 4$, $V = 1635(1)$ Å 3 , $D_c = 1.500$ g cm^{-3} , $R(R_w) = 3.0\%$ (3.8%) for 2349 reflections ($I > 3\sigma(I)$). H-atoms were located from the difference Fourier maps. The heavy atoms were refined anisotropically and the H-atoms

with fixed temperature factors (1.2 times B_{eq} of the host atom). Refinements were performed using TEXSAN software [13]. Figures were plotted on ORTEPII [14].

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