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# X-Ray structures of ethylenebis(tetrahydroindenyl)-titanium and -zirconium dichlorides: a revision

**Scott Collins**★, **Bradley A. Kuntz, Nicholas J. Taylor and David G. Ward**

*Guelph-Waterloo Centre for Graduate Work in Chemistry, Waterloo Campus, Waterloo, Ont., Canada N2L 3G1*

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## Abstract

The structures of both ethylenebis($\eta^5$-tetrahydroindenyl)titanium dichloride (**1**) and its zirconium analog **2** have been redetermined in the centric space group *I*2/*c* (non-standard setting of *C*2/*c*) at room temperature. Arguments are presented that suggest that the original space group (*Cc*) in the published X-ray structures of compounds **1** and **2** was incorrectly selected. An improved modification to the literature route that allows the preparation of multi-gram amounts of **1** and **2** is also described.

## Introduction

Interest in the preparation of chiral *ansa*-metallocene derivatives of the Group 4 transition elements [1–4] has been aroused recently by the discovery that such compounds, i.e. ethylenebis($\eta^5$-tetrahydroindenyl)-titanium and -zirconium dichlorides **1** and **2**, respectively (see Scheme 1) [2,3] serve as precursors to highly active soluble Ziegler–Natta catalysts for the preparation of isotactic polypropylene [5–7].

In connection with a synthetic program aimed to determine the utility of such compounds in asymmetric synthesis, we required major amounts of the title compounds. The existing literature preparations required few steps but proceeded in poor overall yields. We report herein an improved route to the title compounds that facilitates the preparation of multi-gram amounts. During the course of this work the X-ray structures of the title compounds were redetermined in the centric space group *I*2/*c*. We demonstrate here that this space group is apparently the correct one for these compounds by comparision to the structure of compound **1** determined in *Ic*.

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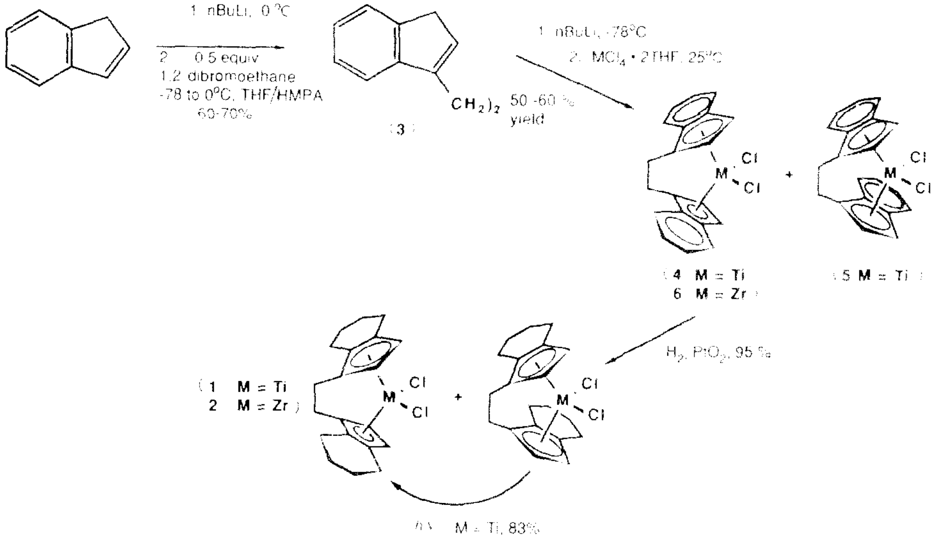
## Results and discussion

### *Synthesis of compounds **1** and **2***

The synthetic route to compounds **1** and **2** is shown in Scheme 1. Since the majority of the steps have been previously reported a lengthy discussion is not warranted. The organic ligand 1,2-di-(3-indenyl)ethane [8] has been prepared in improved yield by reaction of indenyllithium with 1,2-dibromoethane in THF/HMPA. The key step in the syntheses, the preparation of ethylenebis($\eta^5$-indenyl)-titanium and -zirconium dichlorides (compounds **4**, **5** and **6**, Scheme 1) from the dianion of 1,2-bis(3-indenyl)-ethane (**3**) and the appropriate metal tetrachloride proceeds as previously described [2,3]. However, the low yields of titanocene compounds **4** and **5** and zirconocene **6** precludes convenient access to these compounds in useful amounts. The formation of compounds **4**, **5** and **6**, in our hands, was invariably accompanied by the generation of polymeric material which could be removed during the washing steps. We reasoned that bimolecular reactions might be competing successfully with the desired unimolecular formation of the *ansa*-metallocene derivative. Simultaneous slow addition of THF solutions of the dianion of bis(indenyl)ethane and the metal tetrachloride (as the bis THF adduct) to THF with vigorous stirring reduced the amount of byproducts formed and provided satisfactory yields of the desired metallocene derivatives (50 to 60% yields for compounds **4** and **5** or **6**). The remainder of the syntheses proceeded uneventfully although we note that pure racemic compound **1** can be obtained from the initially generated mixture (Step 3, Scheme 1) by recrystallization from toluene. The modification described above allows the large scale economic preparation of these compounds and bodes well for their potential use as chiral reagents or catalysts in organic synthesis.



Scheme 1

### *Crystal data for compounds 1 and 2*

The crystal, intensity collection and refinement data for compounds **1** and **2** are presented in Table 1. In each case because of the much reduced values of $\beta$, the non-standard *I*-centred setting was selected in preference to the *C*-centred cells of the original determinations [2,3]. This follows standard crystallographic practice. Epoxy-coated crystals were mounted on a Syntex $P2_1$ diffractometer equipped with Mo-$K_\alpha$ radiation ($\lambda$ 0.71069 Å). Accurate unit cell constants were determined from 15 general reflections ($20 < 2\theta < 30°$) well distributed in reciprocal space. During the data collections, standard reflections were monitored every 100 measurements; these exhibited only minor fluctuations.

The structures were solved by Patterson and Fourier techniques and refined by full-matrix least squares methods. With $Z = 4$ and the possibility of two-fold symmetry in these compounds, solution in either $Ic$ or $I2/c$ was considered. However, a Wilson plot did not appear to particularly favour either although at low $E$ values, the distribution was more typically centric.

Final positional and isotropic thermal parameters for **1** and **2** in $I2/c$ are collected in Table 2. Bond lengths and angles for compounds **1** and **2** in $I2/c$ are

Table 1

Crystal, intensity collection and refinement data for **1** and **2**

| | **1** | **2** |
|---|---|---|
| Compound formula | $TiCl_2C_{20}C_{24}$ | $ZrCl_2C_{20}H_{24}$ |
| Molecular weight | 383.22 | 426.44 |
| Crystal class | monoclinic | monoclinic |
| $a$ (Å) | 12.340(1) | 12.598(2) |
| $b$ (Å) | 10.088(1) | 10.092(2) |
| $c$ (Å) | 14.144(1) | 14.302(2) |
| $\beta$ (°) | 104.97(1) | 105.38(1) |
| $V$ (Å$^3$) | 1701.0(3) | 1753.2(5) |
| Space group | $I2/c$ | $I2/c$ |
| $\rho_{calc}$ (g cm$^{-3}$) | 1.496 | 1.616 |
| $Z$ | 4 | 4 |
| $F(000)$ | 800 | 872 |
| $T$ (K) | 298 ± 1 | 298 ± 1 |
| $\mu$ (Mo-$K_\alpha$) (cm$^{-1}$) | 8.29 | 9.17 |
| Crystal size (mm) | 0.22 × 0.22 × 0.25 | 0.20 × 0.22 × 0.23 |
| Transmission factors | 0.77–0.86 | 0.76–0.86 |
| Scan method | $\theta-2\theta$ | $\theta-2\theta$ |
| Scan speed (° min$^{-1}$) | 3.45–29.30 | 3.45–29.30 |
| Scan width (°) about $K_{\alpha_1}-K_{\alpha_2}$ | ±0.85 | ±0.85 |
| $2\theta$ range (°) | $(3.2 < 2\theta < 50)$ | $(3.2 < 2\theta < 50)$ |
| Standard reflections | 0.60; 316 | 0.60; 316 |
| Standard variation (%) | ±2 | ±2 |
| Independent reflections | 1508 | 1553 |
| Obs. reflections ($I \geq 3\sigma(I)$) | 1250 | 1443 |
| $R$(final incl. H) [a] | 0.029 | 0.024 |
| $R_w$ [b] | 0.033 | 0.029 |
| Max. residuals (e Å$^{-3}$) | 0.34 | 0.44 |
| Weighting scheme $w^{-1}$ | $1.8 \pm 0.04 \lvert F_o \rvert$ | $2.7 - 0.05 \lvert F_o \rvert + 0.0014 \lvert F_o \rvert^2$ |
| $[\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2/(NO - NV)]^{1/2}$ | 0.37 | 0.42 |

[a] $R = (\Sigma \lvert\lvert F_o \rvert - \lvert F_c \rvert\rvert)/\Sigma \lvert F_o \rvert$. [b] $R_w = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2]^{1/2}/[\Sigma w \lvert F_o \rvert^2]^{1/2}$.

Table 2

Atomic coordinates and isotropic parameters for compounds **1** and **2** in space group $I2/c$

| | Atom | $x$ [a] | $y$ [a] | $z$ [a] | $U_{iso}$ or $U_{eq}$ [b] |
|---|---|---|---|---|---|
| **1** | Ti | 0 | 4877.1(5) | 2500 | 30 |
| | Cl | 475.4(5) | 3325.2(7) | 3777.5(6) | 45 |
| | C(1) | 1116(2) | 6830(2) | 2593(2) | 32 |
| | C(2) | 958(2) | 6198(3) | 1670(2) | 36 |
| | C(3) | 1581(2) | 5008(3) | 1816(2) | 38 |
| | C(3A) | 2102(2) | 4875(2) | 2813(2) | 32 |
| | C(4) | 2933(2) | 3863(3) | 3335(2) | 39 |
| | C(5) | 3681(2) | 4473(3) | 4267(2) | 41 |
| | C(6) | 2991(2) | 5101(3) | 4894(2) | 39 |
| | C(7) | 2266(2) | 6251(2) | 4372(2) | 35 |
| | C(7A) | 1793(2) | 5990(2) | 3300(1) | 29 |
| | C(8) | 622(2) | 8129(2) | 2778(2) | 38 |
| | H(2) | 52(2) | 653(2) | 106(2) | 32(6) |
| | H(3) | 161(2) | 439(3) | 133(2) | 45(7) |
| | H(4X) | 255(2) | 309(2) | 352(2) | 39(7) |
| | H(4Y) | 388(2) | 360(3) | 291(2) | 50(8) |
| | H(5X) | 418(2) | 518(3) | 406(2) | 49(7) |
| | H(5Y) | 416(2) | 379(3) | 464(2) | 44(7) |
| | H(6X) | 251(2) | 435(3) | 508(2) | 44(7) |
| | H(6Y) | 346(2) | 545(2) | 548(2) | 42(7) |
| | H(7X) | 168(2) | 646(3) | 467(2) | 50(8) |
| | H(7Y) | 271(2) | 705(3) | 444(2) | 41(7) |
| | H(8X) | 102(2) | 887(3) | 261(2) | 45(7) |
| | H(8Y) | 69(2) | 826(2) | 344(2) | 31(6) |
| **2** | Zr | 0 | 4806.7(3) | 2500 | 25 |
| | Cl | 492.5(6) | 3230.6(8) | 3837.9(6) | 54 |
| | C(1) | 1129(2) | 6851(2) | 2584(2) | 32 |
| | C(2) | 1005(2) | 6240(3) | 1671(20 | 36 |
| | C(3) | 1627(2) | 5063(3) | 1813(20 | 38 |
| | C(3A) | 2128(2) | 4912(3) | 2810(2) | 33 |
| | C(4) | 2950(2) | 3904(3) | 3331(2) | 40 |
| | C(5) | 3664(2) | 4515(3) | 4264(2) | 42 |
| | C(6) | 2976(2) | 5119(3) | 4871(2) | 39 |
| | C(7) | 2265(2) | 6270(3) | 4360(2) | 35 |
| | C(7A) | 1806(2) | 6014(2) | 3290(2) | 30 |
| | C(8) | 610(2) | 8131(3) | 2777(2) | 39 |
| | H(2) | 58(2) | 655(3) | 108(2) | 34(7) |
| | H(3) | 168(2) | 449(2) | 132(2) | 35(6) |
| | H(4X) | 260(2) | 319(3) | 349(2) | 38(7) |
| | H(4Y) | 340(2) | 365(3) | 292(2) | 44(8) |
| | H(5X) | 412(3) | 523(3) | 411(2) | 51(9) |
| | H(5Y) | 413(2) | 379(3) | 461(2) | 49(8) |
| | H(6X) | 251(2) | 438(3) | 503(2) | 45(7) |
| | H(6Y) | 341(2) | 543(2) | 546(2) | 39(7) |
| | H(7X) | 166(2) | 645(3) | 468(2) | 40(7) |
| | H(7Y) | 270(2) | 701(3) | 443(2) | 48(7) |
| | H(8X) | 99(2) | 885(3) | 262(2) | 48(8) |
| | H(8Y) | 67(2) | 823(3) | 348(2) | 34(7) |

[a] Fractional, $\times 10^4$; $\times 10^3$ for H. [b] $\times 10^3$; ($U_{eq} = \sqrt[3]{U_{11}U_{22}U_{33}}$).

tabulated in Table 3. Anisotropic thermal parameters for **1** and **2** are presented in Table 4. A comparison of selected bond lengths for **1** in both *Ic* and *I*2/*c* and final positional and isotropic thermal parameters and anisotropic thermal parameters for **1** in *Ic* are included as supplementary material (Tables S4–S6, respectively). An ORTEP plot of zirconocene dichloride **2** including all hydrogen atoms is shown in Fig. 1 along with the numbering scheme.

With compound **1**, the refinement in *I*2/*c* proceeded easily and converged with $R = 0.029$ and $R_w = 0.033$. Refinement of **1** in *Ic* also proved possible but it soon became apparent that anisotropic refinement of the carbon atoms resulted in significant anomalies which were further emphasized in the hydrogen atom isotropic thermal parameters. It was also noted that most of the matrix correlation coefficients were in the range 0.85–0.95 and hence strongly suggested a missing symmetry

Table 3

Bond lengths (Å) and angles (°) for **1** and **2**

| | M = Ti | M = Zr | | M = Ti | M = Zr |
|---|---|---|---|---|---|
| M–Cl | 2.3479(8) | 2.4386(8) | M–C(1) | 2.388(2) | 2.490(2) |
| M–C(2) | 2.295(2) | 2.428(3) | M–C(3) | 2.395(2) | 2.510(3) |
| M–C(3A) | 2.516(2) | 2.601(2) | M–C(7A) | 2.479(2) | 2.564(2) |
| C(1)–C(2) | 1.420(3) | 1.415(3) | C(1)–C(7A) | 1.409(3) | 1.416(3) |
| C(1)–C(8) | 1.496(3) | 1.507(4) | C(2)–C(3) | 1.412(4) | 1.408(4) |
| C(3)–C(3A) | 1.397(3) | 1.406(3) | C(3A)–C(4) | 1.499(3) | 1.501(4) |
| C(3A)–C(7A) | 1.421(3) | 1.421(3) | C(4)–C(5) | 1.530(4) | 1.527(4) |
| C(5)–C(6) | 1.518(4) | 1.509(4) | C(6)–C(7) | 1.532(3) | 1.530(4) |
| C(7)–C(7A) | 1.501(3) | 1.508(3) | C(8)–C(8)′ | 1.532(4) | 1.532(4) |
| M–Centroid | 2.096(2) | 2.214(3) | | | |
| C(2)–H(2) | 0.96(2) | 0.93(3) | C(3)–H(3) | 0.94(3) | 0.93(3) |
| C(4)–H(4X) | 0.98(3) | 0.91(3) | C(4)–H(4Y) | 0.96(3) | 0.96(3) |
| C(5)–H(5X) | 1.04(3) | 0.99(3) | C(5)–H(5Y) | 0.97(3) | 0.98(3) |
| C(6)–H(6X) | 1.04(3) | 1.01(3) | C(6)–H(6T) | 0.95(2) | 0.93(3) |
| C(7)–H(7X) | 0.96(3) | 1.00(3) | C(7)–H(7Y) | 0.97(3) | 0.91(3) |
| C(8)–H(8X) | 0.95(3) | 0.93(3) | C(8)–H(8Y) | 0.93(2) | 0.99(3) |
| | M = Ti | M = Zr | | M = Ti | M = Zr |
| Cl–M–Cl′ | 96.36(2) | 98.58(2) | Cl–M–Cent | 105.89(7) | 106.88(7) |
| Cl–M–Cent′ | 107.81(7) | 108.04(7) | Cent–M–Cent′ | 128.47(9) | 125.23(10) |
| M–C(1)–C(2) | 68.79(9) | 70.90(11) | M–C(1)–C(7A) | 76.74(8) | 76.61(9) |
| M–C(1)–C(8) | 118.49(9) | 116.72(10) | C(2)–C(1)–C(7A) | 107.27(13) | 107.28(14) |
| C(2)–C(1)–C(8) | 126.07(13) | 126.57(15) | C(7A)–C(1)–C(8) | 126.63(13) | 126.13(14) |
| M–C(2)–C(3) | 76.40(10) | 76.66(11) | M–C(2)–C(1) | 75.97(9) | 75.70(10) |
| C(1)–C(2)–C(3) | 107.93(13) | 108.26(15) | M–C(3)–C(3A) | 78.31(9) | 77.62(9) |
| M–C(3)–C(2) | 68.63(10) | 70.26(11) | C(2)–C(3)–C(3A) | 108.66(13) | 106.69(15) |
| M–C(3A)–C(3) | 68.76(10) | 70.51(11) | M–C(3A)–C(4) | 129.04(10) | 126.93(11) |
| M–C(3A)–C(7A) | 72.03(8) | 72.59(9) | C(3)–C(3A)–C(4) | 129.82(14) | 129.94(16) |
| C(3)–C(3A)–C(7A) | 107.60(13) | 107.26(14) | C(4)–C(3A)–C(7A) | 122.34(13) | 122.52(15) |
| C(3A)–C(4)–C(5) | 109.52(13) | 109.24(14) | C(4)–C(5)–C(5) | 111.49(13) | 111.74(15) |
| C(5)–C(6)–C(7) | 112.37(12) | 112.67(15) | C(6)–C(7)–C(7A) | 112.33(12) | 111.88(14) |
| M–C(7A)–C(1) | 69.67(9) | 70.90(10) | M–C(7A)–C(3A) | 74.92(9) | 75.48(9) |
| M–C(7A)–C(7) | 124.47(9) | 125.84(10) | C(1)–C(7A)–C(7A) | 108.45(12) | 108.47(14) |
| C(1)–C(7A)–C(7) | 128.02(13) | 128.17(14) | C(3A)–C(7A)–C(7) | 123.07(12) | 122.89(14) |
| C(1)–C(8)–C(8)′ | 108.02(12) | 109.27(14) | | | |

Table 4

Anisotropic thermal parameters ($\times 10^4$) for **1** and **2** in $I2/c$ [a]

| | Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|
| **1** | Ti | 274(3) | 317(3) | 321(3) | 0 | 54(2) | 0 |
| | Cl | 319(3) | 578(5) | 779(5) | −20(3) | 21(3) | 402(4) |
| | C(1) | 308(11) | 333(12) | 324(11) | −71(10) | 60(9) | 31(10) |
| | C(2) | 326(12) | 471(14) | 280(11) | −63(10) | 69(9) | 57(10) |
| | C(3) | 302(12) | 521(14) | 305(11) | −48(11) | 101(9) | −85(11) |
| | C(3A) | 241(11) | 389(13) | 336(11) | −33(10) | 84(9) | −41(10) |
| | C(4) | 298(12) | 447(14) | 432(13) | 50(11) | 52(10) | −72(11) |
| | C(5) | 315(12) | 493(15) | 436(13) | 56(12) | −3(11) | −14(12) |
| | C(6) | 405(13) | 442(14) | 313(11) | 14(12) | −2(10) | −16(10) |
| | C(7) | 377(13) | 347(12) | 315(12) | −20(10) | 36(10) | −42(10) |
| | C(7A) | 256(10) | 304(11) | 313(11) | −53(9) | 70(9) | −9(9) |
| | C(8) | 437(14) | 305(12) | 390(13) | −50(11) | −6(11) | 14(10) |
| **2** | Zr | 221(2) | 269(2) | 226(2) | 0 | 26(1) | 0 |
| | Cl | 353(4) | 608(5) | 733(5) | −32(3) | −6(3) | 399(4) |
| | C(1) | 292(12) | 349(13) | 325(13) | −84(10) | 39(10) | 33(11) |
| | C(2) | 362(13) | 499(16) | 260(13) | −81(12) | 62(10) | 50(11) |
| | C(3) | 313(13) | 566(18) | 316(13) | −48(12) | 121(10) | −89(12) |
| | C(3A) | 232(11) | 437(14) | 342(13) | −37(10) | 82(9) | −55(11) |
| | C(4) | 286(13) | 489(17) | 460(15) | 43(12) | 51(12) | −103(13) |
| | C(5) | 312(13) | 509(17) | 466(15) | 50(12) | −24(12) | 24(13) |
| | C(6) | 420(14) | 443(15) | 313(13) | 5(13) | −15(11) | −13(11) |
| | C(7) | 383(13) | 361(14) | 304(13) | −30(11) | 26(11) | −43(11) |
| | C(7A) | 260(11) | 337(13) | 298(13) | −63(10) | 54(9) | −18(10) |
| | C(8) | 486(16) | 285(14) | 421(14) | −51(12) | 5(13) | 21(11) |

[a] In the form $\exp[-2\pi^2(U_{11}h^2a^{\star 2} + \ldots + 2U_{23}klb^{\star}c^{\star})]$.

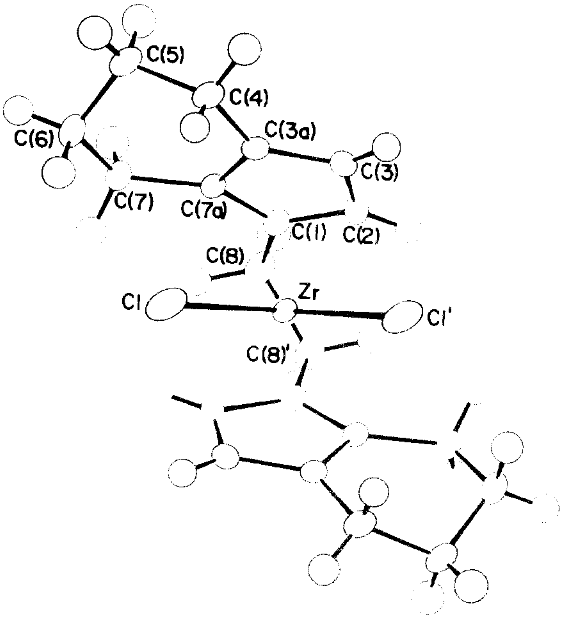


Fig. 1. Molecular structure of [*S*,*S*]-ethylenebis($\eta^5$-tetrahydroindenyl)zirconium dichloride (**2**).

element. In spite of these anomalies, the refinement converged at $R = 0.027$ and $R_w = 0.029$. Inspection of the structure of compound **1** determined in *Ic*, reveals that C–H bond lengths between primed and unprimed atoms are different, as expected, but are in some cases unreasonably different. For example the bond C(7)–H(7X) at 1.19 Å is nearly twice that of C(7)′–H(7X)′ (0.60 Å, see Fig. 1 for numbering). Neither value is of course reasonable for C–H single bond. Similar, though less marked discrepancies are also seen in a number of the Ti–C and C–C distances. It would seem chemically intuitive, based on these results, that *Ic* is not the proper choice of space group for compound **1**.

In compound **2**, refinement in *I2/c* proceeded normally and converged at $R = 0.024$ and $R_w = 0.029$. Accentric refinement of **2** with anisotropic thermal parameters gave several atoms with non-positive definite temperature factors and any attempt to include hydrogen atoms in the refinement just resulted in aimless wandering of these atoms. It proved impossible to reduce the *R* value below 0.05. It was therefore concluded that *I2/c* is the correct space group for both compounds **1** and **2**. Although, a lower value of $R_w$ was obtained by solution of the structure of **1** in space group *Ic*, this is viewed as being the result of increasing the number of parameters from 154 (*I2/c*) to 305 (*Ic*) [9*].

## Experimental

All solvents were reagent grade and were purified as required by distillation. Tetrahydrofuran and toluene were distilled from Na/benzophenone. Dichloromethane and HMPA were dried over and distilled from $CaH_2$. Indene was purified and dried by distillation from $LiAlH_4$ and 1,2-dibromoethane was distilled from $CaCl_2$ immediately prior to use. $TiCl_4 \cdot 2THF$ and $ZrCl_4 \cdot 2THF$ were prepared as described in the literature [10]. Hydrogenations were performed in an Autoclave Engineers stirred pressure reactor. $^1H$ NMR and $^{13}C$ NMR were obtained using a Bruker AM-250 or WP-80 spectrometer. Chemical shifts are recorded in ppm using TMS as an internal standard in $CDCl_3$ solution unless otherwise noted.

### *1. 1,2-Bis(3-indenyl)ethane (3)*

Indene (23.2 g, 0.2 mol) was dissolved in 350 ml of dry THF at 0 °C under argon atmosphere. n-Butyllithium (88 ml of a 2.5 *M* solution in hexane) was added dropwise to the solution over 30 min at this temperature with stirring. HMPA (38 ml, 0.22 mol) was added to the resulting suspension to give a deep brown-red solution. The solution was added cooled to −78 °C (acetone/dry ice bath) and 1,2-dibromoethane (9.5 ml, 0.11 mol) in 50 ml of THF was added dropwise over 1 h by addition funnel. The resulting purple solution was warmed slowly to room temperature and quenched at 0 °C by the addition of saturated $NH_4Cl$ solution (100 ml). The two phase mixture was diluted with petroleum ether (30–60 °C) and the organic layer washed well with water followed by saturated $CuSO_4$ solution to remove HMPA. The organic extract was dried over $MgSO_4$, filtered and concentrated in vacuo to provide an oily solid.

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* Reference numbers with asterisks indicate notes in the list of references.

Crystallization from acetone and ethanol provided 16.8 g (65% yield) of the title compound (m.p. 120–122 °C, lit m.p. [8] 121–122 °C). $^1$H NMR (250 MHz) 7.48 (d, *J* 6.9 Hz, 2H), 7.40 (d, *J* 7.3 Hz, 2H), 7.31 (t, *J* 7.3 Hz, 2H), 7.21 (d, *J* 6.9 Hz, 2H), 6.29 (br s, 2H), 3.35 (br s, 4H), 2.95 (br s, 4H).

### *2. meso- and rac-Ethylenebis($\eta^5$-indenyl)titanium dichloride (**4** and **5**)*

1,2-Bis-3-indenylethane (10 g, 38.7 mmol) was dissolved in 250 ml of dry THF and the solution cooled to − 78 °C. n-Butyllithium (34.0 ml of a 2.5 *M* solution in hexane) was added dropwise over 15 min to the suspension. The pale red suspension was allowed to warm to room temperature at which point the dianion dissolved to give a deep red solution. In a separate flask, 13.0 g of $TiCl_4 \cdot 2THF$ (38.9 mmol) was dissolved in 250 ml of THF. The contents of both flasks were added simultaneously via two cannulae to a third flask containing 100 ml of dry THF with vigorous stirring over ca. 2 h at room temperature. After the addition was complete gaseous HCl was bubbled through the deep brown solution for 30 s and the solvent removed in vacuo to provide a deep green oily solid. The residue was taken up in ether, filtered and washed copiously with ether until the filtrate was nearly colorless. The solid was washed with 4 *M* HCl (10 ml), water (10 ml), ethanol (2 × 10 ml) and ether (2 × 10 ml). The dark brown solid was dried in vacuo to provide 8.7 g (60%) of a mixture of the title compounds. $^1$H NMR (80 MHz): 7.7–7.1 (m, 8H), 6.92 (d, *J* 3.2 Hz), 6.79 (d, *J* 3.2 Hz), 6.48 (d, *J* 3.2 Hz), 6.04 (d, *J* 3.2 Hz, total 4H), 4.05–3.55 (m, 4H).

### *3. rac-Ethylenebis($\eta^5$-tetrahydroindenyl)titanium dichloride (**1**)*

A mixture of *rac*- and *meso*-ethylenebis($\eta^5$-indenyl)titanium dichloride (6.05 g, 16.1 mmol) and $PtO_2$ (250 mg, 1.10 mmol) in 70 ml of dry $CH_2Cl_2$ was hydrogenated at 1000 psi in an stirred reactor for 8 h. The deep red suspension was diluted with additional $CH_2Cl_2$ (300 ml), filtered through Celite and concentrated in vacuo to provide 5.87 g of a mixture of *meso*- and *rac*-ethylenebis($\eta^5$-tetrahydroindenyl)titanocene dichloride (95%). The solid was recrystallized from dry toluene to provide 3.1 g of pure compound **1**. The mother liquor which contained mainly the *meso* diastereomer [11*] was concentrated in vacuo and dissolved in 500 ml of dry THF. The solution was placed in a water-jacketed glass photolysis vessel and irradiated for 6 h using a medium pressure Hg lamp (450 W Hanovia) under nitrogen. During this period crystals of the racemic diastereomer separated out. The mixture was diluted with $CH_2Cl_2$ and then concentrated in vacuo. The red solid was recrystallized from toluene to provide an additional 1.8 g of pure material (83% combined yield). Single crystals of **1** suitable for X-ray diffraction were obtained by cooling a hot saturated toluene solution. $^1$H NMR (250 MHz): 6.60 (d, *J* 3.0 Hz, 2H), 5.57 (d, *J* 3.0 Hz, 2H), 3.49–3.00 (m, 6H), 2.7–2.5 (m, 4H), 2.44–2.30 (dt, *J* 16.5, 5.9 Hz, 2H), 1.96–1.86 (m, 4H), 1.75–1.54 (m, 4H). $^{13}$C NMR (250 MHz): 137.8, 134.7, 128.9, 126.3, 111.5, 27.9, 24.5, 24.2, 21.8 (2C).

### *4. rac-Ethylenebis($\eta^5$-indenyl)zirconium dichloride (**6**)*

The procedure described above for the titanium analog was followed using 5.0 g (19.4 mmol) of 1,2-bis(indenyl)ethane, 7.4 g (19.5 mmol) of $ZrCl_4 \cdot 2THF$ and 17.0 ml of n-butyllithium (2.5 *M* in hexanes) to provide 4.2 g of the title compound (52%) as a bright yellow solid. $^1$H NMR (80 MHz, $C_6D_6$) 7.35–6.75 (m, 8H), 6.46 (d, *J* 3.0 Hz, 2H), 5.76 (d, *J* 3.0 Hz, 2H), 3.01 (s, 4H).

### 5. *rac-Ethylenebis($\eta^5$-tetrahydroindenyl)zirconium dichloride* (**2**)

Compound **5** (4.2 g, 10.0 mmol) and $PtO_2$ (100 mg, 0.44 mmol) in 70 ml of $CH_2Cl_2$ was hydrogenated as described above for the titanium analog. The resulting pale yellow suspension was diluted with $CH_2Cl_2$ (300 ml), filtered through dry Celite and concentrated in vacuo. The residue was dissolved in hot toluene and cooled to provide 2.70 g of the title compound (70%). Single crystals of compound **2** suitable for X-ray diffraction were grown from hot saturated toluene solution. $^1H$ NMR (250 MHz) 6.32 (d, *J* 2.3 Hz, 2H), 5.61 (*d*, *J* 2.3 Hz, 2H), 3.12 (s, 4H), 3.02 (t, *J* 7.0 Hz, 2H), 2.96 (t, *J* 7.1 Hz, 2H), 2.65–2.38 (m, 8H), 2.00–1.80 (m, 2H), 1.65–1.44 (m, 2H). $^{13}C$ NMR (250 MHz) 113.7, 132.1, 124.3, 119.4, 108.5, 28.6, 24.5, 24.3, 22.4, 22.3.

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