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ansa-METALLOCENE DERIVATIVES

XI *. SYNTHESIS AND CRYSTAL STRUCTURE OF A CHIRAL *ansa*-TITANOCENE DERIVATIVE WITH TRIMETHYLENE-BRIDGED TETRAHYDROINDENYL LIGANDS

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Summary

The chiral *ansa*-titanocene derivative 1,3-propanediylbis(4,5,6,7-tetrahydro-1-indenyl)titanium(IV) dichloride has been prepared by reaction of the dilithium salt of 1,3-bis(indenyl)propane with $TiCl_4$ and subsequent hydrogenation. The product has been shown by an X-ray diffraction study to be the R,S metal–ring linkage isomer; in this trimethylene-bridged *ansa*-metallocene the axial symmetry previously observed for the ethylene-bridged congener is destroyed by a non-symmetric location of the $(CH_2)_3$ bridge.

Introduction

Chiral *ansa*-titanocene and *ansa*-zirconocene derivatives with 1,2-ethylene-bridged tetrahydroindenyl ligands [2,3] have been shown to possess interesting properties as pro-catalysts for the isotactic polymerisation of 1-alkenes [4,5]. In a search for related chiral *ansa*-metallocene derivatives, we have prepared a 1,3-propanediyl-bridged homologue, and report here on the changes in the geometry of the ligand framework associated with the increased length of the interannular bridge.

Results and discussion

The required ligand, 1,3-bis(indenyl)propane, was prepared by reaction of 1,3-dibromopropane with indenyllithium in the presence of tetramethylethylenediamine. Reaction of its dilithium salt with $TiCl_4 \cdot 2THF$ in THF and catalytic hydrogena-

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TABLE 1

^{1}H NMR DATA FOR THE DIPOTASSIUM SALT OF 1,3-BIS(INDENYL)PROPANE IN THF-d_8 AND FOR **1** IN BENZENE-d_6 SOLUTION AT ROOM TEMPERATURE

$(CH_2)_3(C_9H_6)_2K_2$ δ (ppm)	$(CH_2)_3(C_9H_{10})_2TiCl_2$ δ (ppm)	Assignment H atoms at	
7.21 (d, 8 Hz, 2H)		$(CH)_4$	C_6 ring
7.01 (d, 8 Hz, 2H)		$(CH)_4$	C_6 ring
6.24 (m, 8 Hz,4H)		$(CH)_4$	C_6 ring
6.36 (d, 3 Hz, 2H)	6.00 (d, 3 Hz, 2H)	$(CH)_2$	C_5 ring
5.53 (d, 3 Hz, 2H)	5.62 (d, 3 Hz, 2H)	$(CH)_2$	C_5 ring
2.99 (t, 7 Hz, 4H)	3.45 (m, 2H)	$(CH_2)_3$	bridge
2.08 (q, 7 Hz, 2H)	2.43 (m, 4H)	$(CH_2)_3$	bridge
	1.92 (m, 4H)	$(CH_2)_4$	C_6 ring
	1.69 (m, 4H)	$(CH_2)_4$	C_6 ring
	1.37 (m, 8H)	$(CH_2)_4$	C_6 ring

tion of the crude product yielded, after recrystallisation from toluene, red crystals of 1,3-propanediylbis(4,5,6,7-tetrahydro-1-indenyl)titanium(IV) dichloride (**1**) in about 11% yield.

The analogous zirconium compound could not be obtained in this manner; hydrogenation of the crude product obtained from the dilithium salt of 1,3-bis(indenyl)propane and $ZrCl_4$ invariably yielded black suspensions from which the zirconocene analogue of **1** could not be separated.

The ^{1}H NMR spectrum in C_6D_6 solution of **1** shows several complex multiplets centered at 3.45, 2.43, 1.92, 1.69 and 1.37 ppm, associated with the trimethylene and tetrahydroindenyl CH_2 protons, and two doublets at 6.00 and 5.62 ppm, due to the vinylic cyclopentadienyl protons (Tab. 1) *. The appearance of only two cyclopentadienyl doublets in its ^{1}H NMR spectrum indicates the presence of only one metal–ring linkage diastereomer of **1**. An X-ray structure analysis showed that **1** is the *R,S*-isomer.

The molecular structure of **1** (Fig. 1) is similar to that previously reported for the trimethylene-bridged titanocene derivative $(CH_2)_3(C_5H_4)_2TiCl_2$ [7,8]. In particular the Ti–Cl and Ti–ring centroid distances, the Cl–Ti–Cl and centroid–Ti–centroid angles (Tab. 2), and the eclipsed conformation of the two C_5 ring ligands of **1** are practically identical to those in $(CH_2)_3(C_5H_4)_2TiCl_2$. In **1**, the trimethylene bridge, the two bridge-head carbon atoms and the Ti centre form a six-membered chelate ring with a boat conformation, whereas in $(CH_2)_3(C_5H_4)_2TiCl_2$ as well as in its Zr congener [9], there is a chair-type conformation of the chelate ring.

In either conformation, the trimethylene bridge apparently requires a sufficiently larger distance between the bridge-head C-atoms than that in an ethylene bridge as to increase the centroid–Ti–centroid angle by about 5° over that of unbridged $(C_3H_5)_2TiCl_2$ [10] and to keep the two bridgehead C atoms and, hence, the two C_5 rings in an eclipsed position. Owing to this conformation, the two $(CH_2)_4$ ring substituents are no longer in equivalent positions, one being placed in a "forward"

* In $CDCl_3$ solution, the separation of the two cyclopentadienyl doublets (5.99 and 5.89 ppm) is only 0.1 ppm; for $(CH_2)_3(C_5H_4)_2TiCl_2$, a splitting of 0.04 ppm in $CDCl_3$ solution was reported [6].

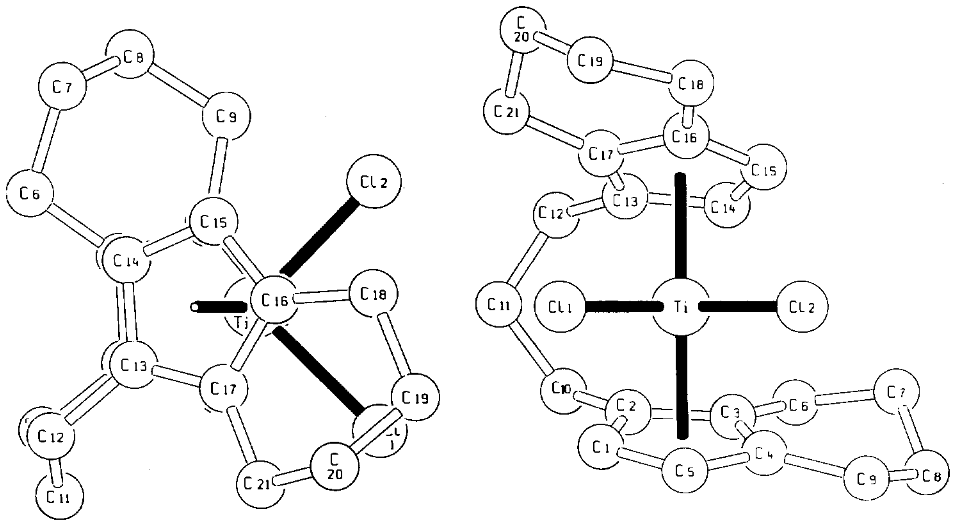

Fig. 1. Molecular structure of **1**. Projection perpendicular to TiCl(1)Cl(2) plane (left) and parallel to TiCl(1)Cl(2) bisector (right).

position, i.e. directly above (or below), the adjacent Cl ligand atom, and the other in a "backward" position, i.e. out of reach for non-bonding interaction with the other Cl atom.

In the crystallographic unit cell of racemic **1**, each of the *R* and *S* enantiomers is represented by two molecules which are related to each other either by a rotation around a C_2 axis or else by a fold-over of the trimethylene bridge to the other side of the molecule. In view of the presence of only two cyclopentadienyl doublets in the ^1H NMR spectrum of **1** it is evident that in solution each of its two enantiomers must undergo rapid structural fluctuation between the two energetically equivalent conformations, so as to generate on the ^1H NMR time scale a pair of equivalent α- and a pair of equivalent β-hydrogen atoms.

TABLE 2

BOND LENGTHS (in pm) AND ANGLES (in degrees) AT THE Ti ATOM IN $(CH_2)_3(C_9H_{10})_2TiCl_2$ (**1**). (CR = centroid of C_5 ring; PL = mean plane of C_5 ring)

Ti–Cl(1)	233.6(4)	Cl(1)–Ti–Cl(2)	92.2(1)
Ti–Cl(2)	234.0(6)	CR(1)–Ti–CR(2)	133.1
Ti–CR(1)	207	PL(1)–PL(2)	47.3
Ti–CR(2)	207	C(2)–C(10)–C(11)	114.2(1.1)
Ti–PL(1)	206	C(10)–C(11)–C(12)	109.9(1.2)
Ti–PL(2)	206	C(11)–C(12)–C(13)	116.2(1.1)
Ti–C(1)	233(1)	Ti–C(13)	238(1)
Ti–C(2)	240(1)	Ti–C(14)	231(1)
Ti–C(3)	246(1)	Ti–C(15)	234(1)
Ti–C(4)	243(1)	Ti–C(16)	243(1)
Ti–C(5)	234(1)	Ti–C(17)	246(1)

Despite this fluctional exchange, it is apparent from Fig. 1 that the two Cl ligand positions are markedly inequivalent at any time, only one of them being sterically shielded by the adjacent tetramethylene ring. Effects of this inequivalence, in which the trimethylene-bridged compound **1** is quite distinct from its axially symmetric ethylene-bridged homologue [2], on its ligand exchange reactions and its catalytic properties are under investigation.

Experimental

All operations were carried out under nitrogen.

1. 1,3-Bis(indenyl)propane. To a solution of 11.6 ml (100 mmol) of indene in 120 ml of petroleum ether were added 62.5 ml of a 1.6 *M* solution (100 mmol) of n-butyllithium in hexane, the mixture was stirred for 1 h at 60°C then cooled to room temperature, and 5 ml (50 mmol) of 1,3-dibromopropane and 2 ml of *N,N'*-tetramethylethylenediamine were added. The mixture was stirred at 60°C for 3 days; then cooled to room temperature, and the resulting suspension was treated with 100 ml of 2 *M* aqueous HCl. The organic layer was separated, washed, successively with water and saturated aqueous $NaHCO_3$ solution, then dried over Na_2SO_4 and evaporated to dryness in vacuo to leave about 12.7 g of a yellow oil. Some 3 g of this oil were transferred to a column (length 40 cm, diameter 2.5 cm) packed with silica gel 60 (Merck, 200–400 mesh). Hexane elution gave several small bands which were discarded, and the main fraction was then eluted with diethyl ether. Evaporation in vacuo yielded 2.2 g (68%) of a yellowish oil which was shown (see 2. below) to be fairly pure 1,3-bis(indenyl)propane.

2. Dipotassium salt of 1,3-bis(indenyl)propane. To a well-stirred suspension of 1 g (25 mmol) of KH in 50 ml THF was added slowly a solution of 2.7 g 1,3-bis(indenyl)propane in 10 ml of THF. When the mixture was allowed to warm to room temperature H_2 was evolved and the mixture became yellow-greenish. It was stirred at room temperature for 3 h, then filtered, and the filtrate was evaporated to dryness and the solid residue washed with n-hexane to yield 2.6 g (74% theoretical yield) of the dipotassium salt of 1,3-bis(indenyl)propane as a greenish powder (for ^1H NMR data see Tab. 1).

3. Dilithium salt of 1,3-bis(indenyl)propane. To a solution of 2.7 g (10 mmol) of 1,3-bis(indenyl)propane in 70 ml of hexane 12.5 ml was added a 1.6 *M* solution (20 mmol) of n-butyllithium in hexane at room temperature. The precipitation of the dilithium salt was completed by stirring for 3 h at 60°C, and the suspension then cooled to room temperature. The supernatant liquid was syphoned off and the residue was washed with a small volume of n-pentane, then dried in vacuo to give 2.0 g (72%) of the dilithium salt of 1,3-bis(indenyl)propane as a white powder.

4. 1,3-Propanediylbis(4,5,6,7-tetrahydro-1-indenyl)titanium(IV) dichloride. Tetrahydrofuran (50 ml) was condensed in vacuo on to 2.6 g (13.7 mmol) of $TiCl_4$ at −80°C. Warming to room temperature led to formation of a yellow suspension of $TiCl_4 \cdot 2THF$, to which a solution of 3.9 g (13.7 mmol) of the dilithium salt of 1,3-bis(indenyl)propane in 20 ml THF was added in one portion. The brown mixture was stirred for 12 h at room temperature then evaporated to dryness, and the residue was stirred for 2 h with 20 ml of CH_2Cl_2 and 15 ml of 4 *M* aqueous HCl in the air. The organic layer was then separated, washed with a small volume of water, dried over Na_2SO_4, and subsequently hydrogenated in a laboratory autoclave

TABLE 3

FRACTIONAL COORDINATES (with esd's) AND ISOTROPIC THERMAL PARAMETERS FOR $(CH_2)_3(C_9H_{10})_2TiCl_2$ (**1**)

Atom	*x*	*y*	*z*	*U*
Ti	0.7595(1)	0.7488(3)	0.9152(2)	
Cl(1)	0.7180(2)	0.9322(4)	1.0267(2)	
Cl(2)	0.7946(2)	0.9713(4)	0.8219(3)	
C(1)	0.8478(7)	0.678(2)	1.0690(9)	0.036(3)
C(2)	0.8310(7)	0.524(2)	1.0167(9)	0.033(3)
C(3)	0.8679(7)	0.536(2)	0.9311(9)	0.035(3)
C(4)	0.9048(7)	0.690(1)	0.9342(8)	0.032(3)
C(5)	0.8920(7)	0.781(2)	1.0175(9)	0.038(3)
C(6)	0.8787(7)	0.397(2)	0.8622(9)	0.038(3)
C(7)	0.9011(9)	0.472(2)	0.772(1)	0.052(4)
C(8)	0.9745(9)	0.590(2)	0.803(1)	0.056(4)
C(9)	0.9575(8)	0.739(2)	0.865(1)	0.046(3)
C(10)	0.7959(7)	0.372(2)	1.0516(9)	0.042(3)
C(11)	0.7056(8)	0.388(2)	1.053(1)	0.049(4)
C(12)	0.6520(9)	0.385(2)	0.947(1)	0.055(4)
C(13)	0.6561(7)	0.538(2)	0.8830(9)	0.036(3)
C(14)	0.6955(8)	0.546(2)	0.8020(9)	0.045(3)
C(15)	0.6749(8)	0.699(2)	0.754(1)	0.045(3)
C(16)	0.6236(7)	0.785(2)	0.8040(9)	0.035(3)
C(17)	0.6121(7)	0.683(2)	0.8832(8)	0.032(3)
C(18)	0.5815(8)	0.949(2)	0.775(1)	0.050(4)
C(19)	0.5301(9)	0.998(2)	0.849(1)	0.059(4)
C(20)	0.4876(8)	0.852(2)	0.881(1)	0.045(3)
C(21)	0.5484(7)	0.726(2)	0.9401(9)	0.040(3)

with ca. 40 mg PtO_2 catalyst under 100 bar H_2 for 30 min. The red mixture was freed from the catalyst by filtration, evaporated to a volume of about 5 ml, mixed with ca. 15 ml toluene, and kept at $-80°C$ overnight. The red-brown precipitate obtained was recrystallised from toluene solution to yield ca. 600 mg (11%) of **1** as red-brown crystals (^1H NMR cf. Tab. 1).

5. Crystal and molecular structure of 1. Space group, cell parameters and X-ray diffraction intensities for a small crystal of **1** were determined on a SYNTEX-P3 four-circle diffractometer at 298 K (Mo-K_α, λ 71.069 pm, graphite monochromator, ω-scan, $\Delta\omega$ 1°, with $3.6 < \dot{\omega} < 29.3°$ min^{-1}, $2 < 2\theta < 44°$). The crystals of **1** are monoclinic, space group $P2_1/c$, a 1678(1), b 796.0(3), c 1367.3(7) pm; β 104.10(5)°. Each unit cell contains 4 crystallographically equivalent molecules (2 enantiomer pairs); V 1771×10^6 pm^3; d_c 1.49 g/cm^3; absorption coefficient μ 8 cm^{-1}. 1541 independent reflections with $I > 4\sigma(I)$ were used for solution and refinement of the structure by use of direct methods (SHELXTL programme), partially anisotropic models, and a weighting scheme based on counting statistics, with H-atoms in calculated positions 100 pm from corresponding C atom. The refinement converged at $R_1 = 0.0954$ and $R_2 = 0.1079$, where $R_1 = (\Sigma \| F_0 | - | F_c \|)/\Sigma | F_0 |$ and $R_2 = [\Sigma(| F_0 | - | F_c |)^2]^{1/2}/[\Sigma | F_0 |^2]^{1/2}$.

Supplementary structural data are available on request from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, upon citation of deposit No. CSD 52109, the names of the authors and the journal reference for this article.

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