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ansa-METALLOCENE DERIVATIVES

VII *. SYNTHESIS AND CRYSTAL STRUCTURE OF A CHIRAL *ansa*-ZIRCONOCENE DERIVATIVE WITH ETHYLENE-BRIDGED TETRAHYDROINDENYL LIGANDS

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Summary

The chiral *ansa*-zirconocene derivative ethylenebis(4,5,6,7-tetrahydro-1-indenyl)-zirconium(IV) dichloride has been prepared by reaction of dilithiobis(indenyl)ethane with $ZrCl_4$ and subsequent hydrogenation. The product has been shown to be the 1-R,S rather than *meso*-metal–ring linkage stereoisomer by an X-ray determination of the molecular structure.

Introduction

Recently we have reported on the synthesis and molecular structure of chiral ethylene-bridged titanocene derivatives [2] containing tetrahydroindenyl ligands, the chirality of which is associated with the metal–ring linkage, and is thus unaffected by exchange of the in-plane ligands, such as occurs, e.g., in catalytic reactions at the Ti centre. Since there are a number of similar catalytic and stoichiometric reactions involving zirconocene compounds (see e.g. ref. 3–12) for which the availability of a chiral catalyst might be useful, we describe here the synthesis of the corresponding ethylenebis(4,5,6,7-tetrahydro-(R,S)-1-indenyl)zirconium(IV) dichloride, en(thind)$_2$-$ZrCl_2$.

Results and discussion

The synthesis of en(thind)$_2$$ZrCl_2$ follows essentially that of the titanium analogue [2]. The tetrahydrofuran (THF) adduct of $ZrCl_4$ was allowed to react for about 2 h at room temperature with the dilithium salt of bis(indenyl)ethane. After treatment of the mixture with HCl gas, evaporation of most of the solvent, and several precipita-

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tion and washing steps (see Experimental), ethylenebis(indenyl)zirconium dichloride (en(ind)$_2$ZrCl$_2$) was obtained as a yellow, air-stable solid in a yield of about 35%. The compound was characterized by its mass spectrum with parent ions at m/e 416–422 showing the expected isotope distribution and by its ^{1}H NMR spectrum (Table 1). Surprisingly, while two metal–ring linkage diastereomers (*meso* and R,S) were found with ethylenebis(indenyl)titanium dichloride [2], only one appeared to be present in the zirconium product, as indicated by the appearance of only one pair of doublets, at δ 6.19 and 6.57 ppm, associated with the two H atoms of the five-membered ring.

Hydrogenation of this product with PtO_2 catalyst in CH_2Cl_2 under 100 bar of H_2 for ca. 30 min yielded, after removal of catalyst, evaporation of solvent, and recrystallization from hot toluene, ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride as colourless, air-stable crystals in about 65% yield. The product was identified by its mass spectrum, which showed the parent ion at m/e 424–430 with the expected isotope distribution, by elemental analysis, and its ^{1}H NMR spectrum (Table 1).

The identity of the product (and by implication that of its unhydrogenated bis-indenyl precursor) as the racemic (R,S) rather than the *meso* isomer was revealed by an X-ray determination of its structure (Fig. 1), which showed the axial symmetry expected for the R,S-isomer. The molecule is isostructural with its titanium analogue [2]; metal–chlorine and metal–ring centroid distances of 244(1) and 221(2) pm, respectively, as well as the Cl–Zr–Cl angle of 98.6(3)° (Table 2), are in accord with those for other zirconocene dihalide derivatives [13,14].

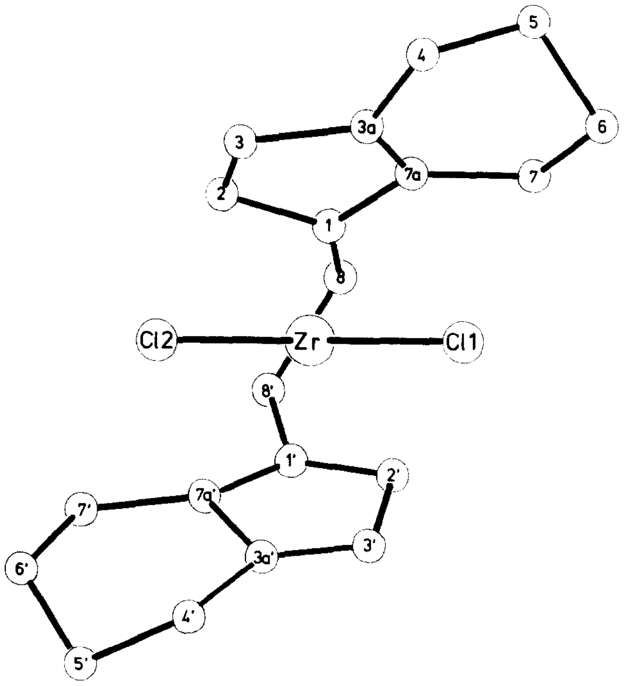

Fig. 1. Molecular structure of R,S-en(thind)$_2$ZrCl$_2$. Atoms not otherwise labelled are C atoms of ligand framework. The figure represents the 1-S-enantiomer.

TABLE 1

^{1}H NMR SPECTRA OF en(ind)$_2$ZrCl$_2$ AND en(thind)$_2$ZrCl$_2$ OBTAINED AT 250 MHz IN CDCl$_3$ AT ROOM TEMPERATURE, SHIFTS δ IN ppm RELATIVE TO δ 7.24 ppm FOR CHCl$_3$

Ethylenebis(indenyl)zirconium dichloride				Ethylenebis(tetrahydroindenyl)zirconium dichloride			
δ(ppm)	Splitting	Integr.	H atoms at	δ(ppm)	Splitting	Integr.	H atoms at
7.1–7.6	m	8	C_6 ring	–	–	–	–
6.57	d, 3.5 Hz	2	C_5 ring (α)	6.32	d, 3 Hz	2	C_5 ring (α)
6.19	d, 3.5 Hz	2	C_5 ring (β)	5.61	d, 3 Hz	2	C_5 ring (β)
3.74	s	4	C_2H_4 bridge	3.1	s	4	C_2H_4 bridge
–	–	–		1.5–3.15	m	16	C_6 ring

TABLE 2

BOND LENGTHS (in pm) AND BOND ANGLES (in degree) AT Zr ATOM IN en(thind)$_2$ZrCl$_2$ (CR = centroid of C_5 ring)

Zr–Cl(1)	2.43(1)	Cl(1)–Zr–Cl(2)	98.6(3)
Zr–Cl(2)	2.45(1)	CR(1)–Zr–CR(2)	125.0
Zr–CR(1)	2.22	Zr–CR(2)	2.21
Zr–C(1)	2.47(2)	Zr–C(1′)	2.51(2)
Zr–C(2)	2.42(1)	Zr–C(2′)	2.50(1)
Zr–C(3)	2.50(1)	Zr–C(3′)	2.53(1)
Zr–C(3A)	2.59(2)	Zr–C(3A′)	2.62(2)
Zr–C(7A)	2.56(2)	Zr–C(7A′)	2.57(2)

The unexpected formation of only the *R,S*-isomer might be correlated with this increased metal–ring distance: with the titanium analogue, en(thind)$_2$TiCl$_2$, the *R,S*-isomer had to be derived by a photoconversion reaction from the *meso*-isomer which, in that case was the kinetically preferred product from the formation of the metal–ring linkage. For the sterically less encumbered zirconium analogue such kinetic control appears to be sufficiently relaxed as to allow direct formation of the more stable *R,S*-isomer.

Experimental

All solvents were thoroughly dried and stored under N_2. $ZrCl_4$ and *S*-binaphthol were obtained from Aldrich, dilithiobisindenylethane was prepared as described in ref. 2.

1. R,S-ethylene-bis(indenyl)zirconium dichloride. About 60 ml of THF were condensed at −196°C into a three-neck flask equipped with a dropping funnel, a reflux condenser and a magnetic stirring bar, containing 4.9 g (21 mmol) $ZrCl_4$. After warming to ca. 60°C under N_2, a solution of the $ZrCl_4$/THF adduct was obtained, and to this was added a solution of 21 mmol of the dilithium salt of bis(indenyl)ethane in 50 ml THF, the excess of the red dianion being kept to a minimum. After stirring at room temperature for 24 h, the yellow precipitate was freed from supernatant solution, repeatedly washed with toluene and dried in vacuo, to yield 3.1 g (35%) of light yellow ethylenebis(indenyl)zirconium dichloride. For characterization see Tables 1 and 2.

TABLE 3

STRUCTURAL PARAMETERS FOR ETHYLENEBIS(4,5,6,7-TETRAHYDRO-1-INDENYL)ZIRCONIUM DICHLORIDE

(a) Fractional coordinates (with esd's) and isotropic thermal parameters

Atom	x/a	y/b	z/c	U	Atom	x/a	y/b	z/c	U
Zr	0.75720	−0.01932(6)	−0.00200		C(8)	0.690(2)	0.316(2)	−0.044(2)	0.050(6)
Cl(1)	0.7080(5)	−0.1795(7)	0.0799(6)		C(1′)	0.873(2)	0.185(1)	0.107(2)	0.029(5)
Cl(2)	0.8060(5)	−0.1743(7)	−0.0894(7)		C(2′)	0.853(1)	0.135(1)	0.176(1)	0.030(4)
C(1)	0.647(2)	0.186(2)	−0.101(2)	0.027(5)	C(3′)	0.925(1)	−0.009(1)	0.232(1)	0.026(4)
C(2)	0.653(1)	0.114(1)	−0.191(1)	0.028(4)	C(3A′)	0.971(2)	−0.004(2)	0.185(2)	0.029(5)
C(3)	0.600(1)	0.021(1)	−0.232(1)	0.028(4)	C(4′)	1.050(1)	−0.124(1)	0.200(1)	0.040(5)
C(3A)	0.545(1)	−0.014(1)	−0.179(1)	0.026(4)	C(5′)	1.128(2)	−0.042(2)	0.190(2)	0.038(5)
C(4)	0.4612(9)	−0.100(1)	−0.221(1)	0.022(3)	C(6′)	1.0609(7)	0.0144(8)	0.0662(7)	0.031(2)
C(5)	0.394(2)	−0.057(2)	−0.192(2)	0.046(6)	C(7′)	0.987(2)	0.128(2)	0.042(2)	0.042(5)
C(6)	0.467(1)	0.009(2)	−0.053(1)	0.039(5)	C(7A′)	0.934(1)	0.108(1)	0.095(1)	0.022(4)
C(7)	0.535(2)	0.125(2)	−0.039(2)	0.025(5)	C(8′)	0.815(1)	0.311(2)	0.027(2)	0.029(5)
C(7A)	0.573(1)	0.094(1)	−0.108(1)	0.025(4)					

(b) Anisotropic thermal parameters [a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zr	0.0193(3)	0.0251(4)	0.0257(3)	0.001(1)	0.0149(3)	−0.001(1)
Cl(1)	0.031(3)	0.055(4)	0.063(4)	0.030(3)	0.023(3)	−0.001(3)
Cl(2)	0.036(4)	0.063(4)	0.077(4)	−0.041(3)	0.037(4)	−0.010(3)

[a] U, U_{ij} in 10^2 pm^2 refer to $T = \exp(-2\pi^2(U_{11}h^2a^{\star 2} + \ldots + 2U_{23}klb^{\star}c^{\star})$.

2. R,S-ethylenebis(tetrahydroindenyl)zirconium dichloride. A suspension of 1 g (2.4 mmol) of *rac*-ethylenebis(indenyl)zirconium dichloride and 75 mg PtO_2 in 25 ml CH_2Cl_2 was hydrogenated in a 100 ml hand autoclave under 100 bar H_2 for 30 min. at room temperature. The mixture was diluted with 500 ml CH_2Cl_2, the catalyst was filtered off and the filtrate was evaporated. The light brown solid residue was thoroughly washed with petroleum ether and recrystallized from hot toluene to yield 650 mg (65%) of *R*,*S*-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium chloride as colourless crystals. Elemental analysis: Found: C, 56.25; H, 5.55. $C_{20}H_{24}ZrCl_2$ calcd.: C, 56.35; H, 5.63%. For further characterization see Tables 1 and 2.

3. Crystal and molecular structure of rac-en(thind)$_2$ZrCl$_2$. Space group, cell parameters and X-ray diffraction intensities were determined on a Syntex-P3 four circle diffractometer at 228 K (Mo-K_α, λ 0.71069 Å, graphite monochromator, ω-scan with $1.8 < \dot{\omega} < 29.3°$ min^{-1} and $2 < 2\theta < 44°$. The crystals of en(thind)$_2$ZrCl$_2$ are monoclinic, space group *Cc*, *a* 1636(1), *b* 1007.7(6), *c* 1430(1) pm; β 132.1°. Each unit cell contains 4 crystallographically equivalent molecules (2 enantiomer pairs); V 1748×10^6 pm^3; d_{calc} 1.62 g/cm^3; absorption coefficient μ 9.2 cm^{-1}. 1057 independent reflections with $F_0 > 2\sigma$ were used for solving and refining the structure, using direct methods (SHELXTL programme), partially anisotropic models and a weighting scheme based on counting statistics. H-atom positions were taken from the Fourier difference map but not refined. The refinement converged at $R_1 = 0.0309$ and $R_2 = 0.0339$, where $R_1 = (\Sigma||F_0| - |F_c||)/\Sigma|F_0|$ and $R_2 = |\Sigma\omega(|F_0| - |F_c|)^2]^{1/2}/[\Sigma\omega|F_0|^2]^{1/2}$. The structural data obtained are available on request from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, under quotation of deposit no. CSD 51351, the authors and the journal reference of this article.

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References

1 H. Schwemlein, L. Zsolnai, G. Huttner and H.H. Brintzinger, J. Organomet. Chem., 256 (1983) 285.
2 F.R.W.P. Wild, J. Zsolnai, G. Huttner and H.H. Brintzinger, J. Organomet. Chem., 232 (1982) 233.
3 T. Yoshida and E. Negishi, J. Am. Chem. Soc., 103 (1981) 4985.
4 W. Kaminsky, Naturwissenschaften, 71 (1984) 93.
5 U. Dorf, K. Engel and G. Erker, Angew. Chem., 94 (1982) 916.
6 D.A. Evans and L.R. McGee, J. Am. Chem. Soc., 103 (1981) 2876.
7 F.W. Hartner, jr., J. Schwartz and S.M. Clift, J. Am. Chem. Soc., 105 (1983) 640.
8 G. Erker, K. Engel, J.L. Atwood and W.E. Hunter, Angew. Chem., 95 (1983) 506.
9 T.N. Sorell, Tetrahedron Lett., 50 (1978) 4985.
10 D.B. Carr and J. Schwartz, J. Am. Chem. Soc., 99 (1977) 638.
11 D.E. van Horn and E. Negishi, J. Am. Chem. Soc., 100 (1978) 2252.
12 R. Choukroun, Inorg. Chim. Acta, 58 (1981) 121.
13 C.H. Saldarriaga-Molina, A. Clearfield and I. Bernal, J. Organomet. Chem., 80 (1974) 79.
14 M.A. Bush and G.A. Sim, J. Chem. Soc. A, (1971) 2225.