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Low-Temperature Crystal Structures of Dichlorobis(η^5-indenyl)zirconium(IV) at 153 K and Dichlorobis(η^5-cyclopentadienyl)zirconium(IV) at 193 K

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The monomeric [$Zr(C_9H_7)_2Cl_2$] complex shares the same overall stereochemistry with [$Zr(C_5H_5)_2Cl_2$]. The molecules in both structures are wedge-like sandwiches with non-parallel rings. The arrangement of four ligands around the zirconium(IV) ion could also be described as a distorted tetrahedron. Dichlorobis(η^5-indenyl)zirconium(IV) crystallizes in the monoclinic space group *Cc*, $a=19.363(12)$, $b=6.968(4)$, $c=11.867(6)$ Å, $\beta=104.62(4)°$, $Z=4$, $V=1549(1)$ Å^3 and dichlorobis(η^5-cyclopentadienyl)zirconium(IV) in the triclinic space group $P\bar{1}$, $a=8.031(4)$, $b=11.768(4)$, $c=12.274(4)$ Å, $\alpha=70.63(3)$, $\beta=103.26(4)$, $\gamma=92.86(2)°$, $Z=4$, $V=1064.7(7)$ Å^3.

The catalytic reactivity of early transition-metal metallocenes with olefins has attracted considerable attention, and metallocene catalysis can be considered a major breakthrough in polyolefin technology.[1] The most common metals used in metallocene catalysts for olefin polymerization are Zr, Ti and Hf. The active catalytic site is an ion-pair: cationic, coordinatively unsaturated metallocene stabilized by a bulky, non-coordinating anion, for example methylaluminoxane (MAO).[1,2] The superior features of metallocene catalysts are: they can polymerize many vinyl monomers; they produce extremely uniform polymers and copolymers; they can control the vinyl unsaturation in the product; they polymerize α-olefins with high stereoregularity.[1,3] This work is a part of our studies on polymerization catalyst precursors based on Group 4 metal compounds.[4–6] In the present paper we report on an X–ray structure determination of a well known dichlorobis(η^5-indenyl)zirconium(IV) complex, hereafter $(Ind)_2ZrCl_2$. For the sake of structural comparison we have also made an accurate low-temperature redetermination of zirconocene, dichlorobis(η^5-cyclopentadienyl)zirconium(IV), Cp_2ZrCl_2.[7]

Experimental

Synthesis. $(Ind)_2ZrCl_2$ was prepared according to the literature procedure and recrystallized from CH_2Cl_2.[8] Cp_2ZrCl_2 was purchased from Aldrich and recrystallized from toluene. These manipulations were made under an argon atmosphere. Toluene was distilled over sodium and dichloromethane over P_2O_5. Tetrahydrofuran used for preparation of $(Ind)_2ZrCl_2$ was dried with $LiAlH_4$.

X-Ray measurements and calculations. Details of the crystal structure analysis, data collection and structure refinement are given in Tables 1 and 2. The $\omega/2\theta$ data collection was carried out with a Rigaku AFC-7S diffractometer using Mo*K*α ($\lambda=0.710\,73$ Å) radiation.[9] The intensities of Cp_2ZrCl_2 were corrected for Lorentz and polarization effects, extinction and absorption (psi-scan, $T=0.88–1.00$). The intensities of $(Ind)_2ZrCl_2$ were corrected for Lp-effects only ($T=0.94–1.00$).[10]

During data collections three check reflections were monitored every 200 reflections, and only statistical fluctuations were observed. The structures were solved and refined using SHELXTL PC and SHELXL programs.[11,12] The structure of $(Ind)_2ZrCl_2$ could be solved and refined only in the space group *Cc*. Scattering factors were those included in SHELXL. All non-hydrogen atoms were anisotropically refined and hydrogen atoms were refined at their calculated positions (riding model). In Cp_2ZrCl_2 the displacement factors of H-atoms were isotropically refined, and in $(Ind)_2ZrCl_2$ they were 1.3 × that of the host atom (riding model).

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Table 1. Crystal data for Cp_2ZrCl_2.

Compound	[$Zr(C_5H_5)_2Cl_2$]
Formula	$C_{10}H_{10}Cl_2Zr$
Formula mass	292.30
Space group	$P\bar{1}$ (No. 2)
Wavelength, $MoK\alpha$/Å	0.71073
Crystal system	Triclinic
Temperature/K	193(2)
a/Å	8.031(4)
b/Å	11.768(4)
c/Å	12.274(4)
α/°	70.63(3)
β/°	103.26(4)
γ/°	92.86(2)
V/Å^3	1064.7(7)
Z	4
D_c/g cm^{-3}	1.823
μ/cm^{-1}	14.83
F(000)	576
Crystal size/mm	0.25 × 0.15 × 0.15
$\theta_{min/max}$/°	2.61/26.50
Reflections collected	4529
Independent reflections	4221 [R(int) = 0.0183]
Refinement method on F^2	Full-matrix least-squares
Data/restraints/parameters	4212 (n)/0/256 (p)
Goodness-of-fit on $F^2(S)$	1.045
Weights	$[\sigma^2(F_o^2)+(0.024P)^2+1.04P]^{-1}$; $P=[\max(F_o^2,0)+2F_c^2]/3$
Final R-indices [$F>4\sigma(F)$]	$R_1=0.0320$, $wR_2=0.0660$
R-indices (all data)	$R_1=0.0373$, $wR_2=0.0688$
Extinction coefficient	0.0012(3)
Residual e-densities/e Å^{-3}	0.415, −0.475

$R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ with $F>4\Sigma$ (F), function minimized is $wR_2=[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)]]^{0.5}$, $S=[\Sigma[w(F_o^2-F_c^2)^2]/(n-p)]^{0.5}$.

Results and discussion

The atomic coordinates for Cp_2ZrCl_2 and $(Ind)_2ZrCl_2$ are presented in Tables 3 and 4; bond lengths and angles are given in Tables 5–8. A structural comparison of geometric parameters in the series of non-bridged $(Ind)_2ZrX_2$ compounds is presented in Table 9. The structure of Cp_2ZrCl_2 consists of two independent monomeric units which very closely resemble each other, whereas $(Ind)_2ZrCl_2$ is composed of single monomer (Figs. 1 and 2). Bradley and Dowell reported the crystal system of Cp_2ZrCl_2, crystallized from benzene, to be monoclinic, $a=6.20$, $b=6.58$, $c=13.33$ Å, $\beta=89.15°$, $Z=2$, $V=544$ Å^3.[13] The volume of this determination is within experimental errors half that reported later by Prout *et al.*,[7] namely $V=1089$ Å^3. Our low-temperature determination shows a contraction of 2.2% in the unit-cell volume compared with that reported by Prout *et al.*, and it is a typical value of contraction when the temperature is decreased from room temperature by 100 °C. The original unit-cell values of Cp_2ZrCl_2 given by Prout *et al.* are published in the Cambridge Structural Database in a reduced Niggli form, $a=8.090$, $b=11.830$, $c=12.363$ Å, $\alpha=71.02$, $\beta=76.89$, $\gamma=87.66°$, $Z=4$, $V=1089$ Å^3, which corresponds to our axis choice except that we have chosen conventionally the maximum

Table 2. Crystal data for $(Ind)_2ZrCl_2$.

Compound	[$Zr(C_9H_7)_2Cl_2$]
Formula	$C_{18}H_{14}Cl_2Zr$
Formula mass	392.41
Space group	Cc (No. 9)
Wavelength, $MoK\alpha$/Å	0.71073
Crystal system	Monoclinic
Temperature/K	153(2)
a/Å	19.363(12)
b/Å	6.968(4)
c/Å	11.867(6)
β/°	104.62(4)
V/Å^3	1549(2)
Z	4
D_c/g cm^{-3}	1.682
μ/cm^{-1}	10.44
F(000)	784
Crystal size/mm	0.40 × 0.20 × 0.10
$\theta_{min/max}$/°	3.12/24.96
Reflections collected	1386
Independent reflections	1386
Refinement method on F^2	Full-matrix least-squares
Data/restraints/parameters	1382 (n)/2/190 (p)
Goodness-of-fit on $F^2(S)$	1.087
Weights	$[\sigma^2(F_o^2)+(0.055P)^2+1.64P]^{-1}$; $P=[\max(F_o^2,0)+2F_c^2]/3$
Final R-indices [$F>4\sigma(F)$]	$R_1=0.0355$, $wR_2=0.0884$
R-indices (all data)	$R_1=0.0373$, $wR_2=0.0903$
Residual e-densities/e Å^{-3}	0.705, −0.771

$R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ with $F>4\sigma$ (F), function minimized is $wR_2=[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)]]^{0.5}$, $S=[\Sigma[w(F_o^2-F_c^2)^2]/(n-p)]^{0.5}$.

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for Cp_2ZrCl_2. U(eq)

Atom	x	y	z	U(eq)[a]
Zr(1)	−1700(1)	7652(1)	1144(1)	24(1)
Zr(2)	−6094(1)	7379(1)	−3926(1)	23(1)
Cl(1)	−4138(1)	6437(1)	658(1)	43(1)
Cl(2)	−2158(1)	9236(1)	−790(1)	40(1)
Cl(3)	−7748(1)	5766(1)	−4473(1)	38(1)
Cl(4)	−6378(1)	8795(1)	−5937(1)	42(1)
C(1)	−1500(6)	7675(4)	3178(3)	56(1)
C(2)	−947(5)	8780(5)	2555(4)	61(1)
C(3)	−2331(7)	9414(4)	1710(4)	60(1)
C(4)	−3742(6)	8701(5)	1800(4)	59(1)
C(5)	−3218(6)	7631(4)	2716(4)	55(1)
C(6)	−207(6)	5830(4)	1125(5)	61(1)
C(7)	298(6)	6799(5)	284(4)	56(1)
C(8)	1275(5)	7520(4)	889(5)	57(1)
C(9)	1319(5)	6980(4)	2082(4)	53(1)
C(10)	389(6)	5960(4)	2219(4)	56(1)
C(11)	−6367(5)	8385(4)	−2489(4)	48(1)
C(12)	−7235(5)	7308(4)	−2193(3)	43(1)
C(13)	−8689(4)	7403(3)	−3100(3)	37(1)
C(14)	−8700(4)	8520(3)	−3985(3)	40(1)
C(15)	−7254(5)	9139(4)	−3597(4)	47(1)
C(16)	−3863(5)	5738(4)	−2854(4)	48(1)
C(17)	−3600(4)	6229(3)	−4016(3)	39(1)
C(18)	−3073(4)	7395(4)	−4177(3)	39(1)
C(19)	−3038(4)	7667(4)	−3149(4)	48(1)
C(20)	−3507(5)	6625(5)	−2320(3)	54(1)

a is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $(Ind)_2ZrCl_2$.

Atom	*x*	*y*	*z*	*U*(eq)[a]
Zr	7487(1)	1630(1)	851(1)	21(1)
Cl(1)	7477(1)	2675(3)	2808(2)	30(1)
Cl(2)	7502(1)	−1786(2)	1307(2)	32(1)
C(1)	8745(5)	3196(13)	1453(9)	33(2)
C(2)	8337(4)	3954(13)	359(8)	38(2)
C(3)	8269(5)	2443(18)	−444(7)	52(3)
C(4)	8552(5)	781(16)	123(9)	50(3)
C(5)	8863(5)	1261(14)	1298(10)	36(2)
C(6)	9263(6)	163(18)	2305(13)	71(4)
C(7)	9527(5)	1183(19)	3332(10)	70(4)
C(8)	9375(6)	3090(19)	3416(10)	67(4)
C(9)	8994(5)	4119(18)	2536(8)	47(2)
C(10)	6197(4)	723(12)	−335(7)	29(2)
C(11)	6594(5)	1548(13)	−1062(7)	37(2)
C(12)	6694(5)	3513(13)	−736(8)	45(2)
C(13)	6444(5)	3815(13)	247(9)	38(2)
C(14)	6127(5)	2121(14)	496(7)	29(2)
C(15)	5752(5)	1636(18)	1352(8)	52(3)
C(16)	5471(5)	−184(19)	1328(8)	63(4)
C(17)	5537(5)	−1529(17)	466(11)	65(4)
C(18)	5889(5)	−1126(14)	−312(9)	45(2)

a U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 5. Selected bond lengths (in Å) for Cp_2ZrCl_2.

Zr(1)–Cl(1)	2.4456(12)	Zr(1)–C(9)	2.477(4)
Zr(1)–Cl(2)	2.4444(13)	Zr(1)–C(10)	2.469(4)
Zr(2)–Cl(3)	2.4498(11)	Zr(2)–C(11)	2.479(3)
Zr(2)–Cl(4)	2.4443(13)	Zr(2)–C(12)	2.478(3)
Zr(1)–C(1)	2.475(4)	Zr(2)–C(13)	2.523(3)
Zr(1)–C(2)	2.468(4)	Zr(2)–C(14)	2.516(3)
Zr(1)–C(3)	2.502(4)	Zr(2)–C(15)	2.498(3)
Zr(1)–C(4)	2.516(4)	Zr(2)–C(16)	2.500(4)
Zr(1)–C(5)	2.501(4)	Zr(2)–C(17)	2.515(3)
Zr(1)–C(6)	2.517(4)	Zr(2)–C(18)	2.513(3)
Zr(1)–C(7)	2.517(4)	Zr(2)–C(19)	2.472(4)
Zr(1)–C(8)	2.498(4)	Zr(2)–C(20)	2.477(4)

Table 6. Selected bond angles (in°) for Cp_2ZrCl_2. Cen(A,B,C,D) refers to the centre of the Cp-ring C(1)–C(5), C(6)–C(10), C(11)–C(15) and C(16)–C(20), respectively.

Cl(2)–Zr(1)–Cl(1)	97.03(5)
Cl(1)–Zr(1)–Cen(A)	105.8(1)
Cl(1)–Zr(1)–Cen(B)	106.4(1)
Cl(2)–Zr(1)–Cen(A)	107.2(1)
Cl(2)–Zr(1)–Cen(B)	106.6(1)
Cen(A)–Zr(1)–Cen(B)	129.2(2)
Cl(4)–Zr(2)–Cl(3)	96.90(4)
Cl(3)–Zr(2)–Cen(C)	106.9(1)
Cl(3)–Zr(2)–Cen(D)	106.4(1)
Cl(4)–Zr(2)–Cen(C)	106.1(1)
Cl(4)–Zr(2)–Cen(D)	106.6(1)
Cen(C)–Zr(2)–Cen(D)	129.3(2)

Table 7. Selected bond lengths (in Å) for $(Ind)_2ZrCl_2$.

Zr–Cl(1)	2.440(2)	Zr–C(5)	2.597(10)
Zr–Cl(2)	2.440(2)	Zr–C(10)	2.616(8)
Zr–C(1)	2.599(9)	Zr–C(11)	2.482(8)
Zr–C(2)	2.482(8)	Zr–C(12)	2.483(8)
Zr–C(3)	2.478(8)	Zr–C(13)	2.487(9)
Zr–C(4)	2.499(9)	Zr–C(14)	2.582(9)

Table 8. Selected bond angles (in °) for $(Ind)_2ZrCl_2$. Cen(A,B) refers to the centre of 5-ring C(1)–C(5), and C(10)–C(14), respectively.

Cl(2)–Zr–Cl(1)	94.71(7)
Cl(1)–Zr–Cen(A)	108.3(2)
Cl(1)–Zr–Cen(B)	105.6(2)
Cl(2)–Zr–Cen(A)	106.5(2)
Cl(2)–Zr–Cen(B)	107.9(2)
Cen(A)–Zr–Cen(B)	128.3(4)

number of obtuse angles. A β-modification of Cp_2ZrCl_2 with a monoclinic space group $P2_1/a$, $a = 13.138$, $b = 14.058$, $c = 13.376$ Å, $\gamma = 117.80$, $Z = 8$, $V = 2185$ Å^3, $T = 295$ K, was published by Soloveichik *et al.*[14] The present Cp_2ZrCl_2 X-ray determination, despite having different Laue symmetry and low-temperature measurements gave similar results compared to the β-modification published before.

When the molecules of Cp_2ZrCl_2 and $(Ind)_2ZrCl_2$ are projected onto their Cl–Zr–Cl planes, they all display a staggered conformation (Fig. 3) as found by Prout *et al.* for Cp_2ZrCl_2,[7] but contrary to their observation, we cannot find any signs of disorder in the Cp_2ZrCl_2 structure. The probable reason for disorder in their study may be a slightly twinning crystal or a real disordered crystal due to different conditions (e.g. solvent) during the crystallization procedure. It is worth mentioning that we had difficulties in finding a good quality single crystal.

In the series of Cp_2ZrX_2 and $(Ind)_2ZrX_2$ complexes, where X is a halide ion, there are parameters that are remarkably invariant. The X–Zr–X angle is almost constant: in Cp_2ZrF_2 96.2(3)°,[15] in Cp_2ZrCl_2 97.03(5) and 96.90(4)°, in β-Cp_2ZrCl_2 97.4 and 96.6 °, in Cp_2ZrI_2 96.2(1)°,[15] and in $(Ind)_2ZrCl_2$ 94.71(7)°. The *ansa* indenyl compounds *rac*-(EBI)$ZrCl_2$ and *meso*-(EBI)$ZrCl_2$, where EBI means ethylenebis(1-indenyl), also have X–Zr–X angles quite close to those in Cp compounds, i.e. 99.09(3) and 97.62(3)°, respectively.[16] The mean values of Zr–C distances are almost independent of X, e.g. 2.50(1) Å for Cp_2ZrF_2, 2.496(4) Å for Cp_2ZrCl_2, 2.48(2) Å for Cp_2ZrI_2, 2.531(9) Å for $(Ind)_2ZrCl_2$, 2.518(2) Å for *rac*-(EBI)$ZrCl_2$ and 2.525(3) Å for *meso*-(EBI)$ZrCl_2$. The individual variation in specific Zr–C distances is within ca. 0.2 Å or less, e.g. 2.50(1)–2.52(1) Å for Cp_2ZrF_2, 2.468(4)–2.523(3) Å for Cp_2ZrCl_2, 2.43(2)–2.51(3) Å for Cp_2ZrI_2, 2.478(8)–2.616(8) Å for $(Ind)_2ZrCl_2$ and 2.438(2)–2.646(3) Å for *rac*- and *meso*-ethylenebis(1-indenyl)zirconium dichlorides. The angles between the planes of the cyclopentadienyl rings are practically independent of X. Also, in the indenyl compounds the angle is constant but ca. 10 ° larger than in Cp compounds. The values are 52.2 ° in Cp_2ZrF_2, 53.38(14) and 53.48(17)° in Cp_2ZrCl_2, 52.5 and 53.1 ° in β-Cp_2ZrCl_2,

Table 9. Geometric parameters in the series of $(Ind)_2ZrX_2$ compounds. Values without e.s.d.'s are calculated using checked data supplied by the Cambridge Structural Database,[25] and they are occasionally different from the values reported in the original papers.

Compound	*a*/Å	*b*/°	*c*/Å	*d*/°	*e*/°	*f*/°	*g*	*T*/K	Ref.
$(Ind)_2ZrMe_2$	2.252	133.0	2.251	96.9	54.2	61.0	s	295	22
$(Ind)_2Zr(CO)_2$	2.196 2.199	145.0	2.221 2.183	86.8	39.2	3.2	e	295	23
$(C_9Me_7)_2ZrCl_2$	2.259(4) 2.255(4)	139.0(4)	2.440(1) 2.419(1)	93.1	28.8	98.5	s	295	24
$(Ind)_2ZrCl_2$	2.230(8) 2.230(8)	128.3(5)	2.440(2) 2.440(2)	94.71(7)	62.07(15)	46.5(3)	s	153(2)	This work

(*a*) Zr–Y distance, where *Y* is the center of the 5-ring. (*b*) Y–Zr–Y angle. (*c*) Zr–X bond length. (*d*) X–Zr–X angle. (*e*) The angle between the indenyl planes of 9 carbon atoms. (*f*) The indenyl rotation angle is formed by the projection of the two lines determined by the centroids of 5- and 6-membered rings on to the X–Zr–X plane, see also Ref. 24. The values are evaluated for simplicity by graphical means with e.s.d. about 0.3°. 180° means fully staggered arrangement and 0° is fully eclipsed. (*g*) configuration, e = eclipsed, s = staggered.

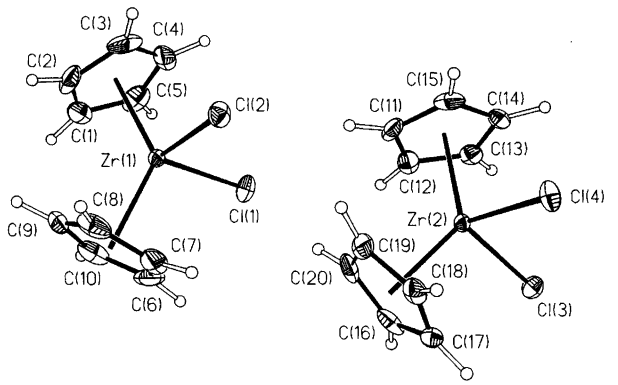

Fig. 1. Two independent monomers of Cp_2ZrCl_2 with atom labels.

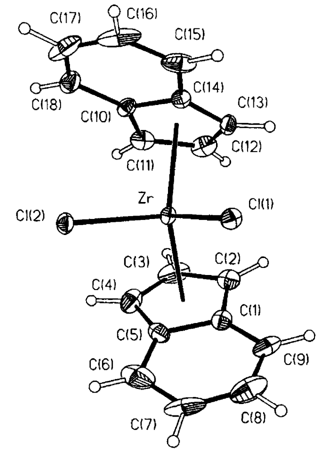

Fig. 2. One monomeric unit of $(Ind)_2ZrCl_2$ with atom labels.

53.7° in Cp_2ZrI_2, 62.07(15)° in $(Ind)_2ZrCl_2$, 63.47(4)° in *rac*-(EBI)$ZrCl_2$ and 62.3(1) in *meso*-(EBI)$ZrCl_2$.

The length of the normal to the cyclopentadienyl ring from the metal atom is a structure invariant that depends on a particular metal atom. In zirconium compounds the value of that length is ca. 2.2 Å,[17] as inevitable also from the actual values for Cp_2ZrF_2 2.21(1) Å, Cp_2ZrCl_2 2.194(4)–2.202(4) Å, β-Cp_2ZrCl_2 2.191–2.201 Å, Cp_2ZrI_2 2.19(2) Å, and $(Ind)_2ZrCl_2$ 2.223(4) Å. The Zr–X distances reflect the ionic radius of the anion X: Cp_2Zr–F 1.975(5) Å,[15] Cp_2Zr–Cl from 2.4443(13) to 2.4498(11) Å, β-Cp_2Zr–Cl 2.437–2.457 Å,[14] $(Ind)_2Zr$–Cl 2.440(2) Å and both (EBI)Zr–Cl from 2.3884(5) to 2.4451(8) Å,[16] and Cp_2Zr–I 2.832(2) Å.[15]

The crystal structures reveal that the overall distorted tetrahedral geometry around the Zr^{IV} is rather constant despite X ions and the cyclopentadienyl moiety. The Zr–C bonds in $(Ind)_2ZrCl_2$ obeys the formula of two long bonds and three shorter bonds leading to a ca. 10° wider angle between the ligands.[18] The two longer bonds from zirconium are connected to those carbon atoms that are common to the five- and six-membered ring. These two common carbon atoms are covalently bonded to three other carbon atoms, which reduces their bonding ability to zirconium. The mutual orientation of indenyl rings in one $(Ind)_2ZrCl_2$ molecule is between the *meso* and *racemic* forms of Et$(Ind)_2ZrCl_2$. If one $(Ind)_2ZrCl_2$ molecule is projected onto the Cl–Zr–Cl plane, the indenyl moieties are projected roughly in a lengthwise manner along the directions of the Zr–Cl bonds (Fig. 3). The opening of the ligand framework leaves the metal centre more exposed, and thus should increase the activity of the metal complex in polymerisations. The other competitive factor is increased steric repulsion around the active centre caused by the indenyl rings. When Cp_2ZrCl_2 was activated with MAO and used in ethylene polymerisation the activity was 82 800 kg PE (mol Zr h bar)$^{-1}$ and analogously 61 900 kg PE (mol Zr h bar)$^{-1}$ for $(Ind)_2ZrCl_2$ with narrow molecular weight distributions 1.9 and 2.2, respectively.[19] According to these results the opening of the ligand framework has only a minor effect on the polymerisation activity compared to steric repulsion of the rotating indenyl rings. The bridge between indenyl fragments increases the activity by reducing the sterical hindrance of the indenyl rings. The activity observed for *rac*-Et$(Ind)_2ZrCl_2$ was 98 800 kg PE (mol Zr h bar)$^{-1}$.[19] Even though Cp_2ZrCl_2 and $(Ind)_2ZrCl_2$ produce only low molecular weight atactic polypropylene[20] the modified non-bridged bisindenyl

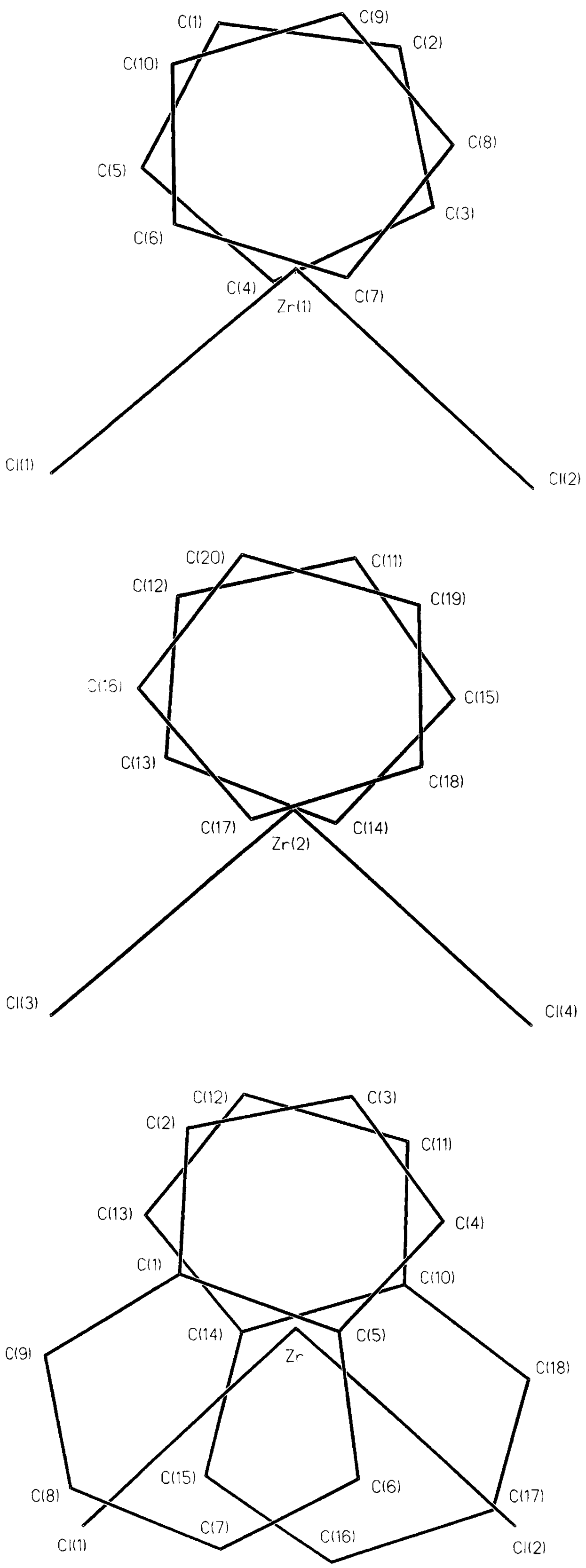

Fig. 3. Ligand molecules in Cp_2ZrCl_2 and $(Ind)_2ZrCl_2$ projected onto the Cl–Zr–Cl plane showing the staggering conformation. H-atoms are omitted for clarity.

complexes have recently achieved new interest. When the rotation of the substituted indenyl fragments is controlled, these zirconium catalyst precursors can be utilised in the production of stereoblock polypropylenes with elastomeric properties.[21]

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