5-Methoxy-substituted zirconium bis-indenyl *ansa*-complexes: synthesis, structure, and the catalytic activity in the polymerization and co-polymerization of alkenes

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SUPPORTING INFORMATION

Crystal structure determination.

The single yellow crystals of **14** were obtained by slow evaporation of saturated chloroform solution of the complex.

Crystal data, data collection, structure solution and refinement are listed in table S1. Absorption correction based on measurements of equivalent reflections was applied.[S1] The structure was solved by direct methods and refined by full matrix least-squares on F^2 [S2] with anisotropic thermal parameters for all non-hydrogen atoms except disordered ^{t}Bu groups and solvent chloroform molecules. Both crystallographically independent ^{t}Bu groups are rotationally disordered over two positions with occupancy ratios 0.68/0.32 and 0.56/0.44. Solvent chloroform molecule is also rotationally disordered around C(30)-H bond over three positions with occupancy ratio 0.45/0.42/0.13.

Table S1. Crystal data, data colection, structure solution and refinement parameters for **14**.

Identification code	**14**
Empirical formula	$C_{54}H_{68}Cl_8O_2SiZr$
Formula weight	1151.99

Color, habit	yellow block
Crystal size, mm	0.20 × 0.10 × 0.10
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions:	
a, Å	29.509(2)
b, Å	9.5058(7)
c, Å	22.7777(17)
α, deg	90
β, deg	113.9980(10)
γ, deg	90
Volume, $Å^3$	5837.0(8)
Z	4
Calculated density, g/cm^3	1.311
Absorption coefficient, mm^{-1}	0.612
F(000)	2392
Diffractometer	Bruker SMART APEX II
Temperature, K	293(2)
Radiation, (lambda, Å)	graphite monochromatized MoK\a (0.71073)
Scan mode	omega
Step per scan, deg	0.5
Scan time, sec	30
θ range, deg	2.27 to 25.50
Limiting indices	$-35 \le h \le 35$, $-11 \le k \le 11$, $-27 \le l \le 27$
Reflections collected / unique	24062 / 5425 [R(int) = 0.0402]
Completeness to θ = 25.50	99.9 %
Reflections with $I>2\sigma(I)$	4403
Absorption correction	Semi-empirical from equivalents
Min. and Max. transmission	0.8874 and 0.9413

Solution method	Direct methods[S2]
Refinement method	Full-matrix least-squares on F^2 (SHELXL-97)[S2a]
Hydrogen treatment	All H atoms were placed in calc. positions and refined using a riding model.
Data / restraints / parameters	5425 / 132 / 294
Goodness-of-fit on F^2	1.084
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0688$, $wR_2 = 0.1881$
R indices (all data)	$R_1 = 0.0853$, $wR_2 = 0.2008$
Largest diff. peak and hole, e/A^3	1.250 and -1.269

Table S2. Atomic coordinates (Å × 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **14**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Zr(1)	10000	2966(1)	2500	30(1)
Cl(1)	9475(1)	4603(1)	2754(1)	49(1)
Si(1)	10000	-477(2)	2500	41(1)
O(1)	8027(1)	4263(5)	1421(2)	59(1)
C(1)	9678(2)	850(5)	1853(2)	35(1)
C(2)	9886(2)	1676(5)	1495(2)	37(1)
C(3)	9599(2)	2888(5)	1262(2)	35(1)
C(4)	9185(2)	2852(5)	1429(2)	35(1)
C(5)	8770(2)	3757(5)	1284(2)	40(1)
C(6)	8423(2)	3380(6)	1514(3)	45(1)
C(7)	8436(2)	2056(6)	1829(3)	48(1)
C(8)	8841(2)	1227(5)	1973(3)	42(1)
C(9)	9231(2)	1594(5)	1792(2)	36(1)

C(10)	10333(2)	1337(6)	1352(3)	50(1)
C(11)	8725(2)	5069(6)	914(2)	41(1)
C(12)	9102(2)	6054(6)	1086(3)	46(1)
C(13)	9049(2)	7303(6)	753(3)	48(1)
C(14)	8617(2)	7619(6)	227(3)	46(1)
C(15)	8245(2)	6621(7)	44(3)	56(2)
C(16)	8293(2)	5372(7)	374(3)	54(2)
C(17)	8551(2)	9031(6)	-133(3)	58(2)
C(18)	8175(4)	9884(13)	20(6)	89(2)
C(19)	8352(4)	8810(14)	-848(4)	89(2)
C(20)	9024(4)	9888(13)	81(6)	89(2)
C(27)	8086(5)	9030(30)	-755(7)	89(2)
C(28)	8533(8)	10270(20)	269(10)	89(2)
C(29)	8995(6)	9190(30)	-304(11)	89(2)
C(21)	7991(3)	1550(6)	1965(3)	70(2)
C(22)	7558(4)	1235(13)	1309(5)	77(2)
C(23)	8126(6)	185(10)	2376(6)	77(2)
C(24)	7820(5)	2652(13)	2335(5)	77(2)
C(31)	8042(7)	-20(11)	2161(7)	77(2)
C(32)	7504(5)	1750(17)	1357(6)	77(2)
C(33)	7970(7)	2457(16)	2518(6)	77(2)
C(25)	8151(3)	5585(9)	1750(4)	80(2)
C(26)	9575(3)	-1642(6)	2692(3)	62(2)
C(30)	9207(1)	6233(5)	4000(3)	93(3)
Cl(11)	8688(2)	7148(7)	3516(4)	113(1)
Cl(12)	9677(2)	7391(6)	4490(3)	113(1)
Cl(13)	9110(2)	4875(6)	4430(3)	113(1)
Cl(14)	9785(2)	6923(7)	4423(3)	113(1)
Cl(15)	8967(2)	5366(7)	4491(3)	113(1)

Cl(16)	8777(2)	7469(8)	3523(4)	113(1)
Cl(17)	8897(6)	4778(14)	4121(10)	113(1)
Cl(18)	9737(5)	6640(20)	4672(7)	113(1)
Cl(19)	8813(6)	7663(14)	3708(10)	113(1)

Table S3. Bond lengths [A] for **14**.

Zr(1)-Cl(1)#1	2.4257(13)	C(12)-C(13)	1.382(8)	C(21)-C(23)	1.555(8)
Zr(1)-Cl(1)	2.4258(13)	C(12)-H(12)	0.9300	C(22)-H(22A)	0.9600
Zr(1)-C(1)#1	2.446(5)	C(13)-C(14)	1.380(7)	C(22)-H(22B)	0.9600
Zr(1)-C(1)	2.446(5)	C(13)-H(13)	0.9300	C(22)-H(22C)	0.9600
Zr(1)-C(2)	2.496(5)	C(14)-C(15)	1.381(9)	C(23)-H(23A)	0.9600
Zr(1)-C(2)#1	2.496(5)	C(14)-C(17)	1.543(8)	C(23)-H(23B)	0.9600
Zr(1)-C(9)#1	2.544(5)	C(15)-C(16)	1.381(8)	C(23)-H(23C)	0.9600
Zr(1)-C(9)	2.544(5)	C(15)-H(15)	0.9300	C(24)-H(24A)	0.9600
Zr(1)-C(3)#1	2.578(5)	C(16)-H(16)	0.9300	C(24)-H(24B)	0.9600
Zr(1)-C(3)	2.578(5)	C(17)-C(28)	1.503(10)	C(24)-H(24C)	0.9600
Zr(1)-C(4)#1	2.641(5)	C(17)-C(19)	1.505(9)	C(31)-H(31A)	0.9600
Zr(1)-C(4)	2.641(5)	C(17)-C(20)	1.517(9)	C(31)-H(31B)	0.9600
Si(1)-C(26)	1.852(6)	C(17)-C(27)	1.519(10)	C(31)-H(31C)	0.9600
Si(1)-C(26)#1	1.852(6)	C(17)-C(29)	1.519(10)	C(32)-H(32A)	0.9600
Si(1)-C(1)#1	1.878(5)	C(17)-C(18)	1.526(9)	C(32)-H(32B)	0.9600
Si(1)-C(1)	1.878(5)	C(18)-H(18A)	0.9600	C(32)-H(32C)	0.9600
O(1)-C(6)	1.383(7)	C(18)-H(18B)	0.9600	C(33)-H(33A)	0.9600
O(1)-C(25)	1.432(9)	C(18)-H(18C)	0.9600	C(33)-H(33B)	0.9600
C(1)-C(2)	1.438(7)	C(19)-H(19A)	0.9600	C(33)-H(33C)	0.9600
C(1)-C(9)	1.452(7)	C(19)-H(19B)	0.9600	C(25)-H(25A)	0.9600
C(2)-C(3)	1.400(7)	C(19)-H(19C)	0.9600	C(25)-H(25B)	0.9600

C(2)-C(10)	1.516(7)	C(20)-H(20A)	0.9600	C(25)-H(25C)	0.9600
C(3)-C(4)	1.419(7)	C(20)-H(20B)	0.9600	C(26)-H(26A)	0.9600
C(3)-H(3)	0.9300	C(20)-H(20C)	0.9600	C(26)-H(26B)	0.9600
C(4)-C(5)	1.422(7)	C(27)-H(27A)	0.9600	C(26)-H(26C)	0.9600
C(4)-C(9)	1.429(7)	C(27)-H(27B)	0.9600	C(30)-Cl(14)	1.711(4)
C(5)-C(6)	1.373(7)	C(27)-H(27C)	0.9600	C(30)-Cl(13)	1.714(4)
C(5)-C(11)	1.481(7)	C(28)-H(28A)	0.9600	C(30)-Cl(11)	1.716(4)
C(6)-C(7)	1.442(8)	C(28)-H(28B)	0.9600	C(30)-Cl(18)	1.730(5)
C(7)-C(8)	1.354(8)	C(28)-H(28C)	0.9600	C(30)-Cl(19)	1.737(5)
C(7)-C(21)	1.545(9)	C(29)-H(29A)	0.9600	C(30)-Cl(17)	1.741(5)
C(8)-C(9)	1.416(7)	C(29)-H(29B)	0.9600	C(30)-Cl(16)	1.746(5)
C(8)-H(8)	0.9300	C(29)-H(29C)	0.9600	C(30)-Cl(15)	1.756(5)
C(10)-H(10A)	0.9600	C(21)-C(31)	1.548(9)	C(30)-Cl(12)	1.767(5)
C(10)-H(10B)	0.9600	C(21)-C(33)	1.548(9)	C(30)-H(30C)	0.9800
C(10)-H(10C)	0.9600	C(21)-C(32)	1.549(9)	C(30)-H(30B)	0.9599
C(11)-C(12)	1.383(8)	C(21)-C(22)	1.549(8)	C(30)-H(30A)	0.9598
C(11)-C(16)	1.395(7)	C(21)-C(24)	1.551(9)	Cl(17)-H(30B)	1.7753

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y,-z+1/2

Table S4. Bond angles [deg] for **14**.

Cl(1)#1-Zr(1)-Cl(1)	100.15(8)	C(3)-C(2)-C(1)	109.5(4)	C(17)-C(20)-H(20B)	109.5
Cl(1)#1-Zr(1)-C(1)#1	122.83(12)	C(3)-C(2)-C(10)	122.5(5)	C(17)-C(20)-H(20C)	109.5
Cl(1)-Zr(1)-C(1)#1	120.90(12)	C(1)-C(2)-C(10)	128.0(5)	C(17)-C(27)-H(27A)	109.5
Cl(1)#1-Zr(1)-C(1)	120.90(12)	C(3)-C(2)-Zr(1)	77.2(3)	C(17)-C(27)-H(27B)	109.5
Cl(1)-Zr(1)-C(1)	122.83(12)	C(1)-C(2)-Zr(1)	71.2(3)	C(17)-C(27)-	109.5

				H(27C)	
C(1)#1-Zr(1)-C(1)	69.3(2)	C(10)-C(2)-Zr(1)	119.8(3)	C(17)-C(28)-H(28A)	109.5
Cl(1)#1-Zr(1)-C(2)	87.56(12)	C(2)-C(3)-C(4)	109.4(4)	C(17)-C(28)-H(28B)	109.5
Cl(1)-Zr(1)-C(2)	132.29(12)	C(2)-C(3)-Zr(1)	70.8(3)	C(17)-C(28)-H(28C)	109.5
C(1)#1-Zr(1)-C(2)	91.32(16)	C(4)-C(3)-Zr(1)	76.7(3)	C(17)-C(29)-H(29A)	109.5
C(1)-Zr(1)-C(2)	33.81(16)	C(2)-C(3)-H(3)	125.3	C(17)-C(29)-H(29B)	109.5
Cl(1)#1-Zr(1)-C(2)#1	132.29(12)	C(4)-C(3)-H(3)	125.3	C(17)-C(29)-H(29C)	109.5
Cl(1)-Zr(1)-C(2)#1	87.56(12)	Zr(1)-C(3)-H(3)	118.9	C(7)-C(21)-C(31)	111.5(9)
C(1)#1-Zr(1)-C(2)#1	33.81(16)	C(3)-C(4)-C(5)	132.7(5)	C(7)-C(21)-C(33)	108.0(9)
C(1)-Zr(1)-C(2)#1	91.32(16)	C(3)-C(4)-C(9)	106.6(4)	C(31)-C(21)-C(33)	109.5(7)
C(2)-Zr(1)-C(2)#1	121.2(2)	C(5)-C(4)-C(9)	120.7(4)	C(7)-C(21)-C(32)	109.8(9)
Cl(1)#1-Zr(1)-C(9)#1	89.38(12)	C(3)-C(4)-Zr(1)	71.8(3)	C(31)-C(21)-C(32)	108.8(7)
Cl(1)-Zr(1)-C(9)#1	131.97(12)	C(5)-C(4)-Zr(1)	124.4(3)	C(33)-C(21)-C(32)	109.2(7)
C(1)#1-Zr(1)-C(9)#1	33.75(16)	C(9)-C(4)-Zr(1)	70.3(3)	C(7)-C(21)-C(22)	107.6(7)
C(1)-Zr(1)-C(9)#1	89.33(16)	C(6)-C(5)-C(4)	117.4(5)	C(7)-C(21)-C(24)	112.9(8)
C(2)-Zr(1)-C(9)#1	94.75(16)	C(6)-C(5)-C(11)	122.0(5)	C(31)-C(21)-C(24)	120.6(11)
C(2)#1-Zr(1)-C(9)#1	54.12(16)	C(4)-C(5)-C(11)	120.6(4)	C(22)-C(21)-C(24)	109.4(6)
Cl(1)#1-Zr(1)-C(9)	131.97(12)	C(5)-C(6)-O(1)	119.8(5)	C(7)-C(21)-C(23)	110.4(7)
Cl(1)-Zr(1)-C(9)	89.37(12)	C(5)-C(6)-C(7)	122.9(5)	C(22)-C(21)-C(23)	109.2(6)
C(1)#1-Zr(1)-C(9)	89.33(16)	O(1)-C(6)-C(7)	117.2(5)	C(24)-C(21)-C(23)	107.3(6)
C(1)-Zr(1)-C(9)	33.76(16)	C(8)-C(7)-C(6)	118.1(5)	C(21)-C(22)-H(22A)	109.5
C(2)-Zr(1)-C(9)	54.12(16)	C(8)-C(7)-C(21)	120.6(5)	C(21)-C(22)-H(22B)	109.5

C(2)#1-Zr(1)-C(9)	94.74(16)	C(6)-C(7)-C(21)	121.2(5)	C(21)-C(22)-H(22C)	109.5
C(9)#1-Zr(1)-C(9)	118.3(2)	C(7)-C(8)-C(9)	121.8(5)	C(21)-C(23)-H(23A)	109.5
Cl(1)#1-Zr(1)-C(3)#1	103.05(11)	C(7)-C(8)-H(8)	119.1	C(21)-C(23)-H(23B)	109.5
Cl(1)-Zr(1)-C(3)#1	79.09(11)	C(9)-C(8)-H(8)	119.1	C(21)-C(23)-H(23C)	109.5
C(1)#1-Zr(1)-C(3)#1	54.86(16)	C(8)-C(9)-C(4)	118.6(5)	C(21)-C(24)-H(24A)	109.5
C(1)-Zr(1)-C(3)#1	121.92(16)	C(8)-C(9)-C(1)	131.8(5)	C(21)-C(24)-H(24B)	109.5
C(2)-Zr(1)-C(3)#1	145.10(16)	C(4)-C(9)-C(1)	109.4(4)	C(21)-C(24)-H(24C)	109.5
C(2)#1-Zr(1)-C(3)#1	31.99(16)	C(8)-C(9)-Zr(1)	124.2(3)	C(21)-C(31)-H(31A)	109.5
C(9)#1-Zr(1)-C(3)#1	52.95(15)	C(4)-C(9)-Zr(1)	77.8(3)	C(21)-C(31)-H(31B)	109.5
C(9)-Zr(1)-C(3)#1	124.97(16)	C(1)-C(9)-Zr(1)	69.4(3)	C(21)-C(31)-H(31C)	109.5
Cl(1)#1-Zr(1)-C(3)	79.09(11)	C(2)-C(10)-H(10A)	109.5	C(21)-C(32)-H(32A)	109.5
Cl(1)-Zr(1)-C(3)	103.05(11)	C(2)-C(10)-H(10B)	109.5	C(21)-C(32)-H(32B)	109.5
C(1)#1-Zr(1)-C(3)	121.92(16)	H(10A)-C(10)-H(10B)	109.5	C(21)-C(32)-H(32C)	109.5
C(1)-Zr(1)-C(3)	54.86(16)	C(2)-C(10)-H(10C)	109.5	C(21)-C(33)-H(33A)	109.5
C(2)-Zr(1)-C(3)	31.99(16)	H(10A)-C(10)-H(10C)	109.5	C(21)-C(33)-H(33B)	109.5
C(2)#1-Zr(1)-C(3)	145.10(16)	H(10B)-C(10)-H(10C)	109.5	C(21)-C(33)-H(33C)	109.5
C(9)#1-Zr(1)-C(3)	124.98(15)	C(12)-C(11)-C(16)	116.8(5)	O(1)-C(25)-H(25A)	109.5
C(9)-Zr(1)-C(3)	52.96(15)	C(12)-C(11)-C(5)	122.3(4)	O(1)-C(25)-H(25B)	109.5
C(3)#1-Zr(1)-C(3)	176.7(2)	C(16)-C(11)-C(5)	120.9(5)	H(25A)-C(25)-	109.5

				H(25B)	
Cl(1)#1-Zr(1)-C(4)#1	79.47(11)	C(13)-C(12)-C(11)	121.8(5)	O(1)-C(25)-H(25C)	109.5
Cl(1)-Zr(1)-C(4)#1	103.60(11)	C(13)-C(12)-H(12)	119.1	H(25A)-C(25)-H(25C)	109.5
C(1)#1-Zr(1)-C(4)#1	54.90(15)	C(11)-C(12)-H(12)	119.1	H(25B)-C(25)-H(25C)	109.5
C(1)-Zr(1)-C(4)#1	120.52(16)	C(14)-C(13)-C(12)	121.4(5)	Si(1)-C(26)-H(26A)	109.5
C(2)-Zr(1)-C(4)#1	124.06(16)	C(14)-C(13)-H(13)	119.3	Si(1)-C(26)-H(26B)	109.5
C(2)#1-Zr(1)-C(4)#1	53.12(16)	C(12)-C(13)-H(13)	119.3	H(26A)-C(26)-H(26B)	109.5
C(9)#1-Zr(1)-C(4)#1	31.93(15)	C(13)-C(14)-C(15)	116.9(5)	Si(1)-C(26)-H(26C)	109.5
C(9)-Zr(1)-C(4)#1	143.79(15)	C(13)-C(14)-C(17)	121.6(5)	H(26A)-C(26)-H(26C)	109.5
C(3)#1-Zr(1)-C(4)#1	31.52(15)	C(15)-C(14)-C(17)	121.5(5)	H(26B)-C(26)-H(26C)	109.5
C(3)-Zr(1)-C(4)#1	148.23(15)	C(16)-C(15)-C(14)	122.2(5)	Cl(14)-C(30)-Cl(13)	109.1(4)
Cl(1)#1-Zr(1)-C(4)	103.60(11)	C(16)-C(15)-H(15)	118.9	Cl(13)-C(30)-Cl(11)	115.9(3)
Cl(1)-Zr(1)-C(4)	79.47(11)	C(14)-C(15)-H(15)	118.9	Cl(14)-C(30)-Cl(19)	105.9(8)
C(1)#1-Zr(1)-C(4)	120.52(16)	C(15)-C(16)-C(11)	120.8(5)	Cl(18)-C(30)-Cl(19)	112.7(4)
C(1)-Zr(1)-C(4)	54.90(15)	C(15)-C(16)-H(16)	119.6	Cl(18)-C(30)-Cl(17)	112.5(4)
C(2)-Zr(1)-C(4)	53.12(16)	C(11)-C(16)-H(16)	119.6	Cl(19)-C(30)-Cl(17)	111.6(4)
C(2)#1-Zr(1)-C(4)	124.06(16)	C(19)-C(17)-C(20)	109.0(6)	Cl(14)-C(30)-Cl(16)	113.4(3)
C(9)#1-Zr(1)-C(4)	143.79(15)	C(28)-C(17)-C(27)	109.1(8)	Cl(17)-C(30)-Cl(16)	109.7(7)
C(9)-Zr(1)-C(4)	31.93(15)	C(28)-C(17)-C(29)	109.2(8)	Cl(14)-C(30)-Cl(15)	112.9(4)

C(3)#1-Zr(1)-C(4)	148.22(15)	C(27)-C(17)-C(29)	107.8(7)	Cl(19)-C(30)-Cl(15)	103.3(9)
C(3)-Zr(1)-C(4)	31.52(15)	C(19)-C(17)-C(18)	108.8(6)	Cl(16)-C(30)-Cl(15)	109.4(3)
C(4)#1-Zr(1)-C(4)	175.3(2)	C(20)-C(17)-C(18)	107.5(6)	Cl(13)-C(30)-Cl(12)	112.2(3)
C(26)-Si(1)-C(26)#1	106.6(4)	C(28)-C(17)-C(14)	112.5(11)	Cl(11)-C(30)-Cl(12)	110.8(3)
C(26)-Si(1)-C(1)#1	113.1(3)	C(19)-C(17)-C(14)	111.4(7)	Cl(15)-C(30)-Cl(12)	107.8(5)
C(26)#1-Si(1)-C(1)#1	114.3(3)	C(20)-C(17)-C(14)	113.3(6)	Cl(18)-C(30)-H(30C)	106.5
C(26)-Si(1)-C(1)	114.3(3)	C(27)-C(17)-C(14)	111.5(11)	Cl(19)-C(30)-H(30C)	106.5
C(26)#1-Si(1)-C(1)	113.1(3)	C(29)-C(17)-C(14)	106.6(11)	Cl(17)-C(30)-H(30C)	106.5
C(1)#1-Si(1)-C(1)	95.6(3)	C(18)-C(17)-C(14)	106.7(7)	Cl(14)-C(30)-H(30B)	106.8
C(6)-O(1)-C(25)	115.6(5)	C(17)-C(18)-H(18A)	109.5	Cl(16)-C(30)-H(30B)	107.6
C(2)-C(1)-C(9)	105.0(4)	C(17)-C(18)-H(18B)	109.5	Cl(15)-C(30)-H(30B)	106.3
C(2)-C(1)-Si(1)	128.0(4)	C(17)-C(18)-H(18C)	109.5	Cl(12)-C(30)-H(30B)	125.8
C(9)-C(1)-Si(1)	123.6(4)	C(17)-C(19)-H(19A)	109.5	Cl(13)-C(30)-H(30A)	106.0
C(2)-C(1)-Zr(1)	75.0(3)	C(17)-C(19)-H(19B)	109.5	Cl(11)-C(30)-H(30A)	105.5
C(9)-C(1)-Zr(1)	76.8(3)	C(17)-C(19)-H(19C)	109.5	Cl(12)-C(30)-H(30A)	105.5
Si(1)-C(1)-Zr(1)	97.5(2)	C(17)-C(20)-H(20A)	109.5		

Symmetry transformations used to generate equivalent atoms: #1 -x+2,y,-z+1/2

Table S5. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **14**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zr(1)	34(1)	25(1)	31(1)	0	13(1)	0
Cl(1)	53(1)	44(1)	44(1)	-7(1)	15(1)	15(1)
Si(1)	49(1)	24(1)	50(1)	0	21(1)	0
O(1)	40(2)	69(3)	64(3)	9(2)	19(2)	14(2)
C(1)	41(3)	28(2)	38(2)	-5(2)	17(2)	-3(2)
C(2)	41(3)	37(3)	33(2)	-7(2)	15(2)	-2(2)
C(3)	40(3)	35(3)	30(2)	-1(2)	13(2)	-3(2)
C(4)	37(2)	35(3)	30(2)	-2(2)	11(2)	-4(2)
C(5)	33(2)	45(3)	34(2)	-1(2)	7(2)	-2(2)
C(6)	37(3)	50(3)	43(3)	1(2)	13(2)	3(2)
C(7)	43(3)	56(3)	44(3)	3(2)	18(2)	-6(3)
C(8)	45(3)	37(3)	45(3)	1(2)	20(2)	-8(2)
C(9)	37(2)	34(2)	33(2)	-4(2)	10(2)	-3(2)
C(10)	54(3)	52(3)	52(3)	-3(3)	31(3)	7(3)
C(11)	35(3)	44(3)	39(3)	3(2)	10(2)	4(2)
C(12)	39(3)	48(3)	41(3)	4(2)	6(2)	3(2)
C(13)	45(3)	44(3)	46(3)	4(2)	9(2)	-3(2)
C(14)	47(3)	50(3)	38(3)	6(2)	15(2)	8(2)
C(15)	43(3)	63(4)	43(3)	12(3)	-1(2)	7(3)
C(16)	42(3)	56(4)	49(3)	7(3)	5(2)	-4(3)
C(17)	59(4)	56(4)	48(3)	15(3)	10(3)	8(3)
C(25)	74(5)	79(5)	92(5)	-11(4)	37(4)	22(4)
C(26)	71(4)	35(3)	78(4)	6(3)	30(4)	-10(3)
C(30)	125(7)	90(6)	89(6)	-9(5)	68(6)	0(5)

Table S6. Hydrogen coordinates (Å × 10^4) and isotropic displacement parameters (Å^2 × 10^3) for **14**.

	x	y	z	U(eq)
H(3)	9669	3605	1033	43
H(8)	8863	394	2198	50
H(10A)	10263	526	1078	74
H(10B)	10613	1147	1747	74
H(10C)	10405	2124	1141	74
H(12)	9399	5871	1435	55
H(13)	9309	7944	886	58
H(15)	7953	6795	-314	68
H(16)	8034	4726	235	64
H(18A)	7867	9380	-123	133
H(18B)	8122	10776	-195	133
H(18C)	8299	10033	476	133
H(19A)	8597	8334	-953	133
H(19B)	8277	9705	-1062	133
H(19C)	8056	8251	-986	133
H(20A)	9280	9336	35	133
H(20B)	9126	10154	523	133
H(20C)	8966	10718	-180	133
H(27A)	8080	8194	-996	133
H(27B)	8087	9843	-1005	133
H(27C)	7799	9048	-659	133
H(28A)	8809	10220	680	133
H(28B)	8229	10241	328	133
H(28C)	8550	11123	56	133
H(29A)	9056	8310	-469	133
H(29B)	9282	9443	73	133

H(29C)	8928	9905	-625	133
H(22A)	7663	554	1079	116
H(22B)	7462	2086	1062	116
H(22C)	7281	870	1379	116
H(23A)	8170	-574	2126	116
H(23B)	7864	-44	2507	116
H(23C)	8429	330	2750	116
H(24A)	7652	3410	2051	116
H(24B)	8104	3012	2690	116
H(24C)	7598	2215	2493	116
H(31A)	8076	-576	1829	116
H(31B)	7752	-314	2220	116
H(31C)	8330	-143	2555	116
H(32A)	7532	1286	999	116
H(32B)	7445	2735	1266	116
H(32C)	7232	1352	1430	116
H(33A)	8255	2261	2907	116
H(33B)	7674	2238	2577	116
H(33C)	7968	3435	2412	116
H(25A)	7896	5849	1888	120
H(25B)	8179	6291	1465	120
H(25C)	8461	5501	2117	120
H(26A)	9765	-2331	3002	92
H(26B)	9355	-2107	2307	92
H(26C)	9386	-1091	2865	92
H(30C)	9317	5969	3662	112
H(30B)	9242	5530	3719	112
H(30A)	9333	5812	3714	112

Table S7. Hydrogen bonds for **14** [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(30)-H(30A)...Cl(1)	0.96	2.65	3.592(8)	167.5

Symmetry transformations used to generate equivalent atoms: #1 -x+2,y,-z+1/2

Preparation of the catalysts.

All the catalyst solutions were prepared following the same recipe: Al/Zr molar ratio = 600 - 800, MAO/TIBA = 2, total concentration of zirconocene ~0.5-1 g/l. *Catalyst system **19***. 39.1 mL of TIBA isododecane solution (90 g/l) were mixed with 7.4 ml of MAO toluene solution (Albemarle 30% wt, d = 0.928 g/ml, 35.5 mmol). The solution was stirred for 1 h at room temperature and transferred into a 50 mL Schlenk flask containing compound **19** (55.8 mg,40.2 μmol). The resulting mixture was diluted with 9.8 ml of isododecane to give a cloudy orange solution. Final concentration of metallocene- 0.99 g/l. *Catalyst system **19***. 39.1 mL of TIBA isododecane solution (90 g/l) were mixed with 7.4 ml of MAO toluene solution (Albemarle 30% wt, d = 0.928 g/ml, 35.5 mmol). The solution was stirred for 1 h at room temperature and transferred into a 50 mL Schlenk flask containing compound **19** (55.8 mg, 88.7 μmol). The resulting mixture was diluted with 9.8 ml of isododecane to give a cloudy orange solution. Final concentration of metallocene- 0.99 g/l. *Catalyst system **15a***. Prepared by the same manner using 32.2 ml of TIBA isododecane solution, 6.1 ml of MAO toluene solution (29 mmol), and 15 (58.5 mg, 73 mmol). The final solution was diluted with 8.2 mL of isododecane to reach a concentration of metallocene 1.26 g/l. The resulting orange mixture contained some gelly precipitate which was removed by decantation. *Catalyst system **13b***. Prepared using 13.7 ml of TIBA cyclohexane solution, 3.3 ml of MAO toluene solution (15.6 mmol), and **13** (46.9 mg, 58.5 μmol). The final solution was diluted with 18.7 ml of cyclohexane to give a cloudy orange solution. Final concentration of metallocene = 1.313 g/l. *Catalyst system **13c***. Prepared using 14.5 ml of TIBA isododecane solution (110 g/l), 3.4 ml of MAO toluene solution (16.1 mmol), and **13** (24.2 mg, 30 μmol). The resulting mixture was diluted with 18.6 ml of

isododecane to give a bright orange solution. Final concentration of metallocene = 0.663 g/L. *Catalyst system **19***. Prepared using 13.5 ml of TIBA cyclohexane solution, 3.2 ml of MAO toluene solution (15.3 mmol), and **19** (28.4 mg, 38.3 μmol). The final solution was diluted with 7.7 ml of cyclohexane to give a dark red solution. Final concentration of metallocene = 1.165 g/l.

Polymerization procedure.

*Propylene polymerization. Catalyst system **18***. A 4.4 L jacketed stainless-steel autoclave, equipped with a mechanically driven stirrer and a 35-mL stainless-steel vial and connected to a thermostat for temperature control, was previously purified by washing with an $Al(i\text{-}Bu)_3$ solution in hexane and dried at 50 °C in a stream of nitrogen. 6 mmol of $Al(i\text{-}Bu)_3$ (as a 100 g/L solution in hexane), 629 g of cyclohexane, and 732 g of propylene were charged at room temperature, in order to obtain in the polymerization conditions, a liquid composition 50/50 propylenelcyclohexane (wt/wt). The autoclave was then thermostated at the polymerization temperature, 100 °C, corresponding for this composition at a pressure of 30.5 bar-g. 5 mL of the *catalyst system **18*** containing the catalyst/cocatalyst mixture (0.99 mg metallocene1mL solution) was injected in the autoclave by means of 4 mL of cyclohexane through the stainless-steel vial. Propylene was continuously fed for 30 minutes to maintain the pressure at 30.5 bar-g for a total consumption of 44 grams of propylene. The pressure into the autoclave was decreased until 20 bar, the bottom discharge valve was opened and the polymer was discharged into a heated steel tank containing water at 70°C. The tank heating was switched off and a flow of nitrogen at 0.5 bar-g was fed. After cooling at room temperature, the steel tank was opened and the wet polymer collected. The wet polymer was dried in an oven under reduced pressure at 70 °C.

The procedure was repeated feeding 693 g of cyclohexane and 677 g of propylene in order to obtain, at 120°C and 36 bar-g, a liquid composition of 50/50 % wt propylene/cyclohexane. 5 mL of the *catalyst system **18*** containing the catalyst/cocatalyst mixture (0.99 mg metallocene/mL solution) was injected in the autoclave by means of 4 mL of cyclohexane through the stainless-steel vial. Propylene was

continuously fed for 30 minutes to maintain the pressure of 36 bar-g: 19.6 g of propylene were consumed.

*Propylene polymerization. Catalyst system **13a***. The procedure described for comparative example with catalyst **18** was repeated feeding 732 g of cyclohexane and 820 g of propylene in order to obtain a liquid composition at 100 °C, 32 bar-g, corresponding to a liquid composition of 50/50 % wt propylene/cyclohexane. 4 mL of the catalyst system 15a containing the catalyst/cocatalyst mixture (0.629 mg metallocene/mL solution) was injected in the autoclave by means of 4 mL of cyclohexane through the stainless-steel vial. Propylene was continuously fed for 30 minutes to maintain the real pressure of 32 bar-g: 14 g of propylene were consumed. The polymer was discharged according to the procedure described for comparative example with catalyst **18**.

The procedure was repeated feeding 693 g of cyclohexane and 677 g of propylene in order to obtain a liquid composition at 120 °C, 36 bar-g, corresponding to a liquid composition of 35/75 % wt propylene/cyclohexane. 2.5 mL of the *catalyst system 13a* containing the catalyst/cocatalyst mixture (1.26 mg metallocene/mL solution) was injected in the autoclave by means of 4 mL of cyclohexane through the stainless-steel vial. Propylene was continuously fed for 30 minutes to maintain the real pressure of 36 bar-g: 16 g of propylene were consumed.

*Ethylene/propylene copolymerization. Catalyst system 13**b***. The procedure was performed feeding 945 g of cyclohexane, 118 g of ethylene, and 172 g of propylene in order to obtain, at 100 °C and 31 bar-g, a liquid composition of 18/82 % wt monomers/cyclohexane. 300 normal mL of hydrogen were charged in the autoclave. 0.8 mL of the *catalyst system **13b*** containing the catalyst/cocatalyst mixture (1.313 mg metallocene/mL solution) were diluted with 5 mL of cyclohexane, charged in the stainless-steel vial and injected into the autoclave by nitrogen overpressure. A constant ethylenelpropylene mixture 70/30 % wt was continuously fed for 30 minutes to maintain the pressure of 31 bar-g: 65.5 g of ethylene and 28 g of propylene were consumed. The polymer was discharged according to the procedure described in the comparative example for *catalyst system **18***.

*Ethylene/propylene copolymerization. Catalyst system **13c**.*The procedure was repeated feeding 716 g of cyclohexane, 61 g of ethylene and 631 g of propylene in order to obtain a liquid composition at 100 °C, 36 bar-g, corresponding to a liquid composition of 8/92 % wt ethylene/propylene. 2 mL of the *catalyst system **15c*** containing the catalyst/cocatalyst mixture (0.663 mg metallocene/mL solution) was injected in the autoclave by means of 4 mL of cyclohexane through the stainless-steel vial. A constant ethylenelpropylene mixture 17/83 % wt was continuously fed for 30 minutes to maintain the pressure of 36 bar-g: 26 g of ethylene and 126 g of propylene were consumed.

*Ethylene/propylene copolymerization. Catalyst system **19**.* The procedure was repeated feeding 1000 g of cyclohexane, 142.5 g of ethylene, and 137 g of propylene in order to obtain, at 100 °C and 33 bar-g, a liquid composition of 15/85 % wt monomers/cyclohexane. 3 mL of the *catalyst system **19*** containing the catalyst/cocatalyst mixture (1.165 mg metallocene/mL solution) were diluted with 5 mL of cyclohexane, charged in the stainless-steel vial and injected into the autoclave by nitrogen overpressure. A constant ethylenelpropylene mixture 70/30 % wt was continuously fed for 30 minutes to maintain the pressure of 33 bar-g: 48 g of ethylene and 20.9 g of propylene were consumed.

Polymer analysis.

Intrinsic viscosity (IV) in tetrahydronaphthalene. The measurement were done in tetrahydronaphthalene (THN) solution obtained by dissolving the polymer at 135 °C for 1 hour.

Melting temperature (T_m). Calorimetric measurements were performed by using a differential scanning calorimeter DSC Mettler. The instrument is calibrated with indium and tin standards. The weighted sample (6-8 mg), was sealed into aluminum pans, heated to 200 °C and kept at that temperature for 5 minutes, then cooled at 20 °C/min to 5 °C, kept 5 minutes at 5 °C, then finally heated to 200°C at a rate of 20 °C/min. In this second heating run, the peak temperature was assumed as melting temperature (T_m) and the area as the global melting enthalpy (ΔH).

Gel permeation chromatography (GPC). Gel permeation chromatography was carried out at 135 °C in 1,2,4-trichlorobenzene using a GPC apparatus 150C from Waters.

^{13}C NMR measurement. The polymer microstructure was investigated by ^{13}C NMR analysis. The samples were dissolved with a 8% wt/v concentration in 1,1,2,2-tetrachloroethane-d_2 at 120 °C. The ^{13}C NMR spectra were acquired at 120 °C on a Bruker DPX400 spectrometer operating at 100.61 MHz. In the case of isotactic polypropylene, the *mmmm* peak at 21.8 ppm was used as internal reference, and the pentad distribution and amounts of regioerrors were determined as described.[S3] In the case of ethylene-propylene copolymers, each spectrum was acquired with a 90° pulse, 12 seconds of delay between pulses and CPD (WALTZ 16) to remove ^{1}H-^{13}C coupling. About 1500 transients were stored in 32K data points using a spectral window of 6000 Hz. The assrgnments of the peaks were made accordrng lo Randall[S4a] and Tritto[S4b], and the triad distribution and copolymer compositions was deternined accordmg lo Kakugo.[S5] The $S_{\delta\delta}$ peak at 29.9 ppm was used as internal reference. The product of recativity ratios $r_1 \times r_2$ was calculated from the triads according to Carman.[S6]

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