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Synthesis and olefin polymerization performance of new *ansa*-zirconocene with OSiO-bridged bis(2-indenyl) ligand

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General

Synthesis of ligands was carried out in argon atmosphere using standard Schlenk techniques. Synthesis of complexes was conducted using glove-box (Vacuum Atmospheres Co.). All reagents and solvents were supplied from commercial sources unless otherwise stated. Hydrocarbon solvents (toluene, hexane, methylcyclohexane) and $CDCl_3$ were stored over MS 4Å for at least 24 h prior to use. Diethyl ether was stored over solid KOH for 24 h and then refluxed over and distilled from sodium/benzophenone. Triethylamine was stored over MS 4Å for 24 h prior to use. Amount of residual water in dry organic solvents was determined by means of Karl Fischer Coulometer C20 (Mettler Toledo). The values were always less than 10 ppm. NMR spectra were recorded at Bruker AVANCE 400 with carrier frequency 400 MHz with the use of TMS as standard for chemical shifts. C, H microanalyses were conducted at Heracus Analyzer CHN-O-Rapid.

Synthesis

*Bis(1H-inden-2-yloxy)dimethylsilane (Si(O-2-Ind)$_2$) (**1**)*. To a solution of NaI (15.0 g, 99.0 mmol, 1.1 eq) in MeCN (200 ml), Me_2SiCl_2 (5.6 ml, 45.0 mmol, 0.5 eq) was added, and the resulting mixture was stirred for 30 min (protection from light was needed). To the mixture freshly distilled indan-2-one (12.0 g, 90.0 mmol, 1 eq) was added followed by dropwise addition of Et_3N (13.8 ml, 99.0 mmol, 1.1 eq). The reaction mixture was stirred for 3 h and extracted three times with pentane. The combined extracts were evaporated to dryness under reduced pressure. Yield of the title product (yellow oil) of ca. 90% purity (NMR) was 20.5 g (71%). HRMS: calc. for $[M+H]^+$ 321.1306; found 321.1308. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32 (d, 2H, J = 7.3 Hz), 7.20-7.27 (m, 4H), 7.11 (td, 2H, J = 7.2 Hz, J = 1.4 Hz), 6.03 (s, 2H), 3.45 (s, 4H), 0.52 (s, 6H).

*[μ-Bis(η^5-1H-inden-2-yloxy)dimethylsilylene]zirconium dichloride (Si(O-2-Ind)$_2$ZrCl$_2$) (**2**)*. To a solution of bis(1*H*-inden-2-yloxy)dimethylsilane (**1**) (10.0 g, 31.0 mmol, 1 eq) in ether (200 ml), a solution of $(Me_3Si)_2NK$ (12.4 g, 62.0 mmol, 2 eq) in ether (100 ml) was added dropwise at room temperature, and the resulting mixture was stirred for 24 h. After cooling to -78°C, $ZrCl_4(THF)_2$ (11.7 g, 31.0 mmol, 1 eq) was added in one portion, and the resulting mixture was stirred for 48 . The mixture was evaporated to dryness, the residue was extracted with toluene (3×200 ml), and the combined fractions were evaporated to dryness. The crude product was purified by recrystallization from toluene at -30°C. Yield of the title product (yellow solid) was 3.43 g (23%). Calc for

$C_{20}H_{18}Cl_2O_2SiZr$: C (49.99%), H (3.78%). Found: C (50.10%), H (3.92%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50 (dd, 4H, *J* = 6.5 Hz, *J* = 3.2 Hz), 7.10 (dd, 4H, *J* = 6.5 Hz, *J* = 3.2 Hz), 5.75 (s, 4H), 0.20 (s, 6H).

*[μ-Bis(η^5-1H-inden-2-yl)dimethylsilylene] dimethylzirconium (**3**)***. Butyllithium solution in hexanes (2.80 ml, 7.00 mmol, 2 eq) was added dropwise to a solution of di(1*H*-inden-2-yl)dimethylsilane [S1] (1.00 g, 3.50 mmol, 1 eq) in dry ether (30 ml) at -80°C. The resulting mixture was stirred at room temperature overnight and then cooled to -80°C. Zirconium tetrachloride (0.80 g, 3.50 mmol, 1 eq) was added in one portion to the mixture, and the resulting yellow suspension was stirred at room temperature overnight. The mixture was evaporated to dryness, and toluene (40 ml) was added followed by MeMgBr solution in ether (12.0 ml, 35.0 mmol, 10 eq), and the reaction mixture was stirred at 80°C overnight. The resulting solution was evaporated to dryness, the residue was redissolved in toluene and filtered through a short pad of Celite. The filtrate was concentrated, the precipitated yellow crystalline powder was filtered off, washed with hexane and dried *in vacuo* to afford the title product as yellow crystalline powder in 45% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55 (dd, 4H, *J* = 6.5 Hz, *J* = 3.2 Hz), 7.07 (dd, 4H, *J* = 6.5 Hz, *J* = 3.2 Hz), 5.90 (s, 4H), 0.39 (s, 6H), -0.85 (s, 6H).

Polymerization

Polymerization experiments. All pre-catalysts were tested in ethene homopolymerization and ethene/1-hexene copolymerization under a standard set of conditions, using a setup of high-throughput reactors previously described [S2,S3] and used extensively in various polymerization studies [S4-S6]. The polymerization was carried out in toluene at 80°C and at constant pressure of ethene (65±1 psi_g, fed in a semi-batch fashion). Two different concentration of 1-hexene were explored, namely 10.0 % v/v and 40.0 % v/v. In all cases, methylaluminoxane (MAO) was used as a scavenger and activator (Al/Zr = 2300-11500).

The copolymer samples were characterized by gel permeation chromatography (GPC) for the determination of the molar masses and molecular weight distributions.

Detailed procedure: The polymerizations were carried out in a Parallel Pressure Reactor (PPR48). This equipment, containing 48 reactors mounted in a triple glove-box, was sold commercially by the company Symyx, thereafter by the company Freeslate. The applied polymerization protocols were as follows.

Prior to the execution of a library, the 48 PPR cells (reactors) undergo ‘bake-and-purge’ cycles overnight (8 h at 90-140°C with intermittent dry N_2 flow) to remove any contaminants and left-overs from previous experiments. After cooling to glove-box temperature, the stir tops are taken off, and the cells are fitted with disposable 10 ml glass inserts and PEEK stirring paddles (previously hot-dried under vacuum); the stir tops are then set back in place, the cells are loaded with the proper amounts of toluene (in the range 2.0-4.0 ml), 1-hexene (when needed, 0.5 or 2.0 ml) and MAO solution (100 μl of 0.1 mol dm^{-3} in toluene), thermostated at 80°C, and brought to the operating pressure of 65 psi_g with ethylene. At this point, the catalyst injection sequence is started; the proper volumes of a toluene ‘chaser’, a solution of the precatalyst in toluene (typically in the range 0.005 - 0.01 mmol dm^{-3}), and a toluene ‘buffer’ are uptaken into the slurry needle, and then injected into the cell of destination. The reaction is left to proceed under stirring (800 rpm) at constant temperature and pressure with continuous feed of ethylene for 30 min, and quenched by over-pressurizing the cell with dry air (preferred to other possible catalyst poisons because in case of cell or quench line leaks oxygen is promptly detected by the dedicated glove-box sensor).

After quenching, the cells were cooled down and vented, the stir-tops are removed, and the glass inserts containing the reaction phase are taken out and transferred to a Genevac EZ2-Plus centrifugal evaporator, where all volatiles are distilled out and the polymers are thoroughly dried overnight. Reaction yields are double-checked against on-line monomer conversion measurements by robotically weighing the dry polymers in a Bohdan Balance Automator while still in the reaction vials (subtracting the pre-recorded tare). Polymer aliquots are then sampled out for the characterizations.

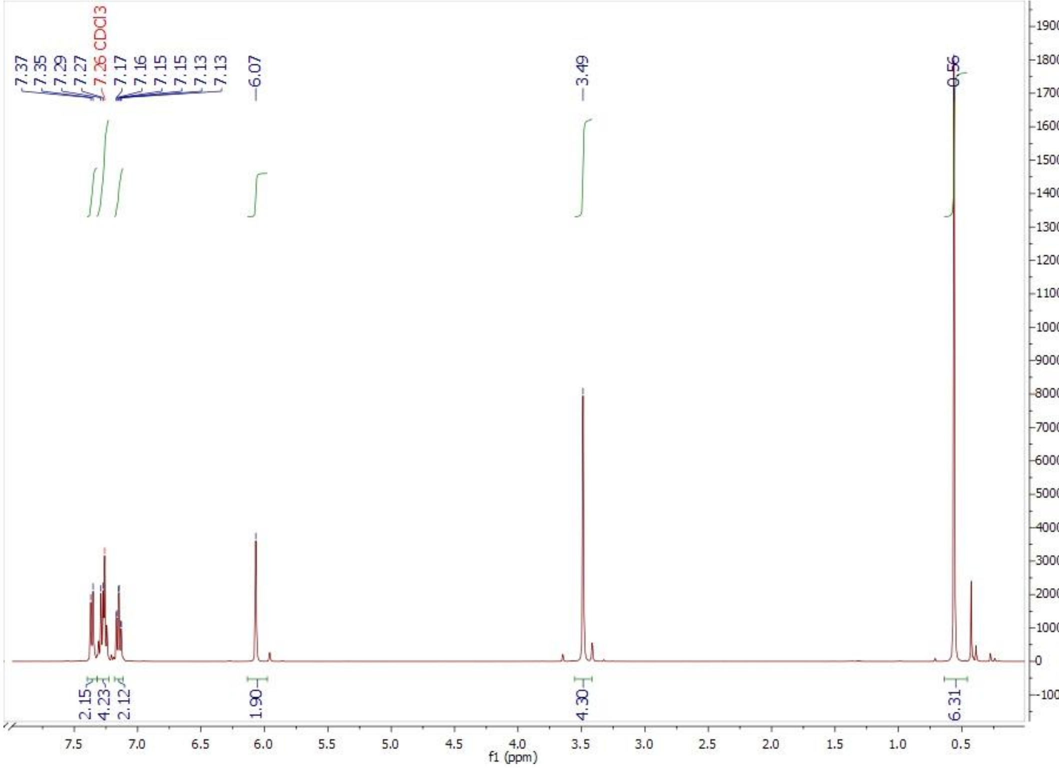
Table S1. Full results of ethylene homopolymerization and ethylene/1-hexene copolymerization data for zirconocenes **2**, **3**, and **6**.[a]

Catalyst	***H* (vol%)**	**n_{cat} (nmol)**	***t* (s)**	**Yield (mg)**	**Activity[b]**	**M_n (kDa)**	**M_w (kDa)**	**PDI**	**H_{cop} (mol%)**
2	0	1.0	1800	123	1276	146	378	2.6	-
		1.0	1801	129	1140	148	382	2.5	-
	10.0	3.0	1801	45	127	63	156	2.5	0.5
		2.5	1802	38	126	61	133	2.2	0.5
	40.0	3.0	1801	31	86	44	93	2.1	1.8
		5.0	1802	59	98	45	94	2.1	2.2
3	0	1.0	1801	51	421	3	6	2.0	-
		1.0	1801	111	921	3	6	2.0	-
	10.0	1.0	1801	113	939	3	6	2.0	1.5
		1.5	1801	85	469	3	6	2.0	1.4
	40.0	4.0	1800	70	145	3	6	2.0	5.4
		4.0	1802	74	155	3	6	2.0	6.2
6	0	0.5	1801	24	390	47	109	2.3	-
		1.0	1802	62	596	45	107	2.4	-
	10.0	0.5	1800	52	867	44	91	2.1	0.4
		0.8	1802	60	941	44	92	2.1	0.5
	40.0	0.8	1801	55	573	35	70	2.0	2.0
		1.0	1802	76	636	35	72	2.1	1.8

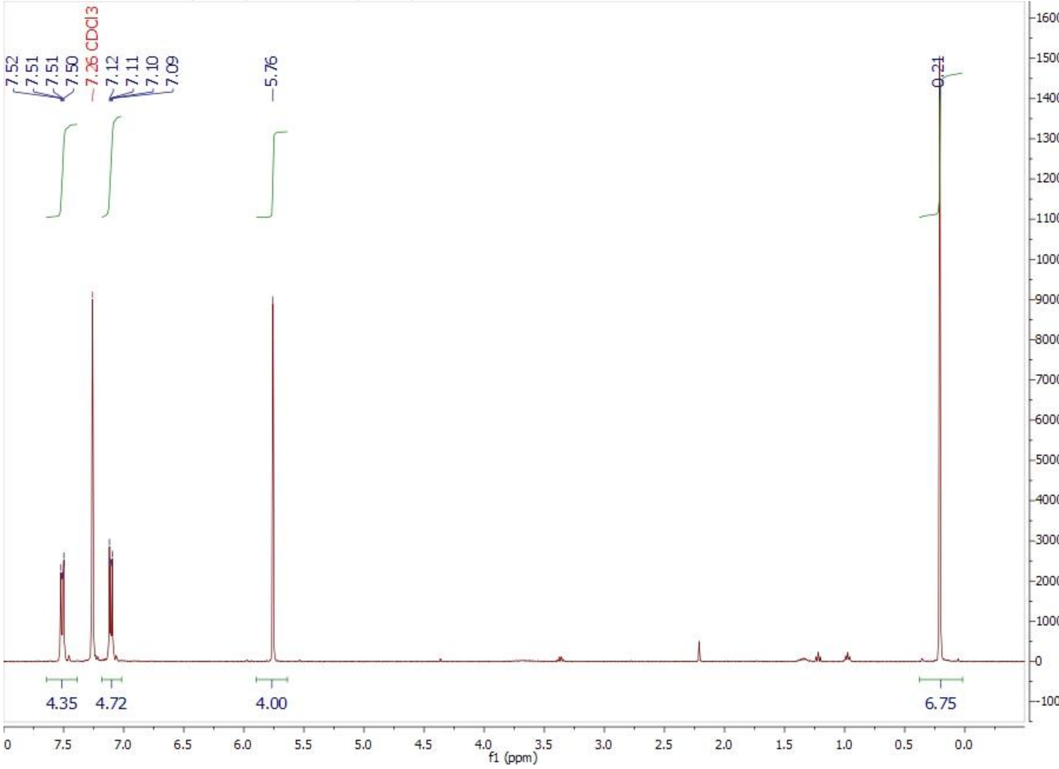
[a] polymerization conditions: P_{total} = 65 psi; T = 80 °C; t = 30 min, [Al] = 2.0 mM, [b] vol% of hexene in the feed, [c] in kg·mmol^{-1}·[C$_2$H$_4$]$^{-1}$·h^{-1}, [d] in kDa, [e] M_w/M_n; [f] mol.% of the incorporated hexene units

NMR spectra

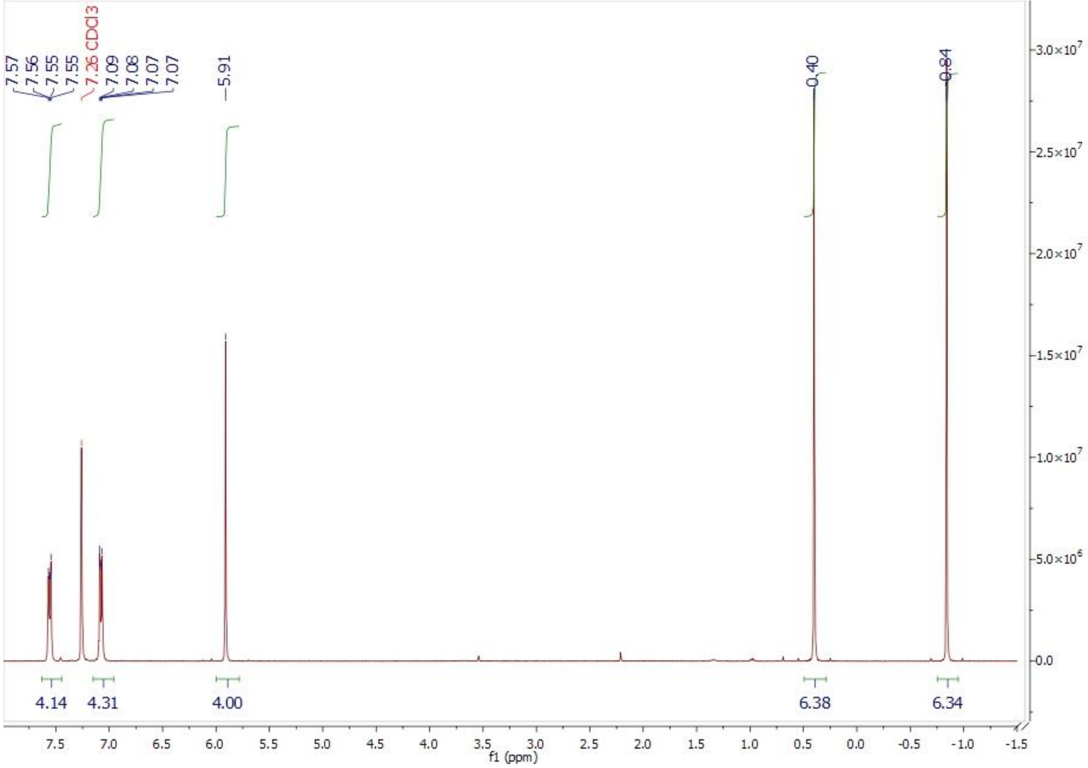
*Bis(1H-inden-2-yloxy)dimethylsilane (Si(O-2-Ind)$_2$) (**1**)*



*[μ-Bis(η^5-1H-inden-2-yloxy)dimethylsilylene]zirconium dichloride (Si(O-2-Ind)$_2$ZrCl$_2$) (**2**)*



*[μ-Bis(η^5-1H-inden-2-yl)dimethylsilylene]dimethylzirconium (Si(2-Ind)$_2$ZrMe$_2$) (**3**)*



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[S2] V. Busico, R. Cipullo, A. Mingione and L. Rongo, *Ind. Eng. Chem. Res.*, 2016, **55**, 2686.

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Crystal data for 2 were collected on a Bruker Apex II CCD diffractometer with MoKα radiation (λ = 0.71073 Å) using the φ- and ω-scan techniques. The structures were solved and refined by direct methods using SHELX. Data were corrected for absorption effects using the multi-scan method (SADABS). All non-hydrogen atoms were refined anisotropically using SHELX. The coordinates of the hydrogen atoms were calculated from geometrical positions.

Table S2. Crystal data and structure refinement for **2**.

Empirical formula	C20 H18 Cl2 O2 Si Zr	
Formula weight	480.55	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C c	
Unit cell dimensions	a = 17.0381(8) Å	α = 90°.
	b = 10.2952(5) Å	β = 125.6830(10)°.
	c = 13.9766(10) Å	γ = 90°.
Volume	1991.4(2) Å^3	
Z	4	
Density (calculated)	1.603 Mg/m^3	
Absorption coefficient	0.892 mm^{-1}	
F(000)	968	
Crystal size	0.24 x 0.20 x 0.18 mm^3	
Theta range for data collection	2.47 to 30.18°.	
Index ranges	-24<=h<=24, -14<=k<=14, -19<=l<=19	
Reflections collected	16357	
Independent reflections	5841 [R(int) = 0.0186]	
Completeness to theta = 30.18°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.609 and 0.436	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5841 / 2 / 238	
Goodness-of-fit on F^2	1.152	
Final R indices [for 5803 rfln with I>2sigma(I)]	R1 = 0.0210, wR2 = 0.0489	
R indices (all data)	R1 = 0.0212, wR2 = 0.0491	
Absolute structure parameter	0.63(2)	
Largest diff. peak and hole	0.641 and -0.387 e.Å^{-3}	