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# Synthesis of zirconium(III) complex by reduction of $O[SiMe_2(\eta^5\text{-}C_5H_4)]_2ZrCl_2$ and its selectivity in catalytic dimerization of hex-1-ene

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## Contents



**General experimental remarks.** All synthetic experiments were performed under purified argon atmosphere. Metallocene synthesis was performed by using standard Schlenk technique. Butyllithium (1.6 *M* solution in hexanes) and zirconocene dichloride were used as purchased (Aldrich). Diethyl ether and THF were refluxed with Na/benzophenone and distilled prior to use. Pentane and hexanes were refluxed over Na/K alloy for 12 hours and then distilled. $CH_2Cl_2$ was washed with aqueous $Na_2CO_3$, stirred with $CaCl_2$ powder, refluxed over $CaH_2$ for 8 h and distilled. $CDCl_3$ (Cambridge Isotope Laboratories, Inc., D 99.8 %) was distilled over $P_2O_5$ and stored over 4 Å molecular sieves. $CD_2Cl_2$ (Cambridge Isotope Laboratories, Inc., D 99.5 %) was stored over $LiAlH_4$ and re-condensed into NMR tube. THF-$d_8$ (Cambridge Isotope Laboratories, Inc., D 99.5 %) was stored over Na/benzophenone and re-condensed into NMR tube. The $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (400 MHz) at 20 °C. The chemical shifts are reported in ppm relative to the solvent residual peaks. Elemental analysis (C, H) was made on a Perkin Elmer Series II CHNS/O Analyzer 2400.

The distribution of 1-hexene oligomers produced was measured by gas chromatography on a KRISTALL-2000M instrument equipped with a SolGel-1ms (60m×0.25mm×0.25μm) column and a flame ionization detector. Helium was used as a carrier gas at a rate of 1.364 ml $min^{-1}$ and with a split ratio of 73.3:1. The injector temperature was 320 °C, and the column temperature was 200 °C within 5 min and then increased from 200 °C to 300 °C at a rate of 10 °C/min.

Zirconocene **2** was prepared according to previously reported procedure [J. Graeper, G. Paolucci and R. D. Fischer, *J. Organomet. Chem.*, 1995, **501**, 211.].

Synthesis and characterization of bis[μ-oxobis(dimethylsilylene-$\eta^5$-cyclopentadienyl)(μ-chloro)zirconium(III)] (complex **3**)

$^1$H NMR spectrum of **2** is provided in Figure S1 for comparison.

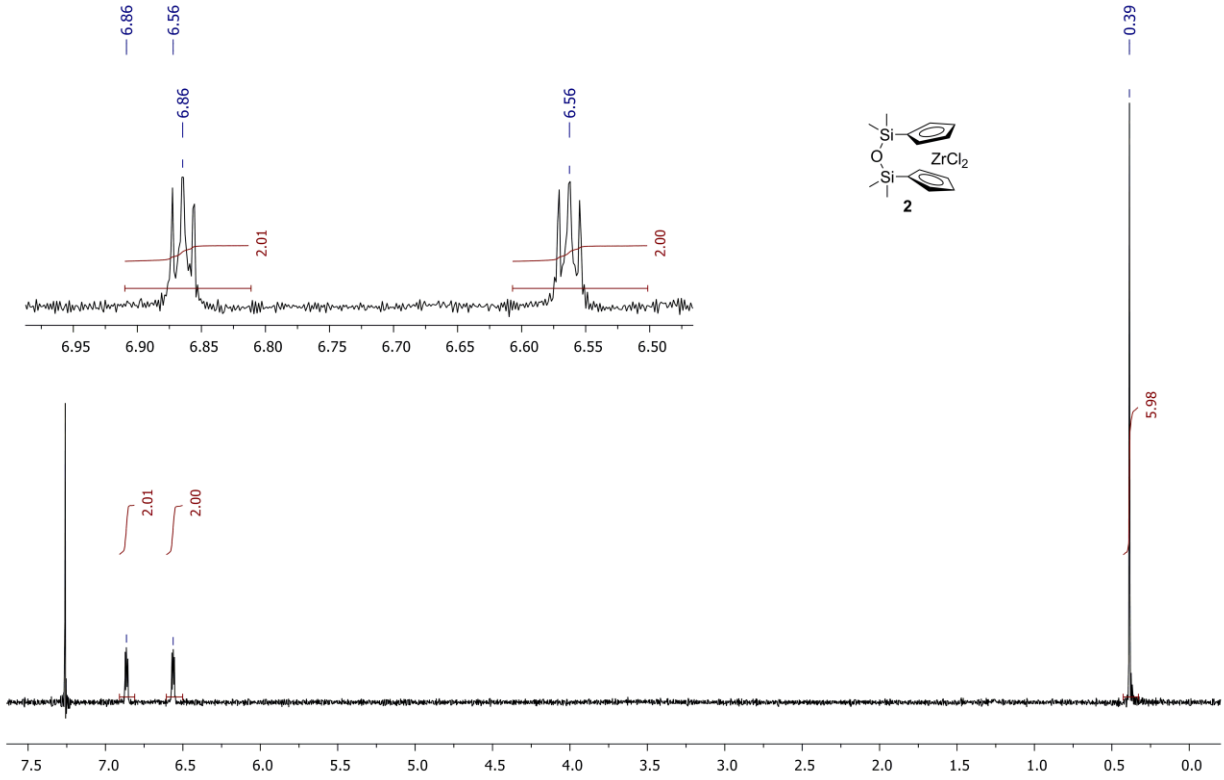


**Figure S1**. $^1$H NMR spectrum ($CDCl_3$, 20 °C) of $O[SiMe_2(\eta^5\text{-}C_5H_4)]_2ZrCl_2$ (**2**).

Zirconium complex **2** (0.30 g, 0.71 mmol) was dissolved in dry THF (2 ml). A filtered solution of $LiAlH_4$ [prepared from $LiAlH_4$ (8 mg, 0.21 mmol) and ether (2 ml)] was added dropwise at 0 °C. The obtained deep purple solution was cooled to –25 °C to afford after one week purple crystals of **3**, which were separated by decantation and dried *in vacuo*. The yield was 0.16 g (56%). Several single crystals were taken for X-ray analysis. For $C_{28}H_{40}Cl_2O_2Si_4Zr_2$, 774.30 calc., %: C 43.43, H 5.21, O 4.13; found, %: C 43.30, H 5.28, O 4.10. $^1$H NMR (THF-$d_8$, 20 °C) δ: 6.41 (bs, 2H); 6.15 (bs, 2H); 5.94 (bs, 2H); 5.45 (bs, 2H); 0.31 (s, 6H); 0.24 (s, 6H). $^{13}$C NMR (THF-$d_8$, 20 °C) δ: 114.14; 108.86; 106.93; 105.94; 105.71; 1.60; 0.97.

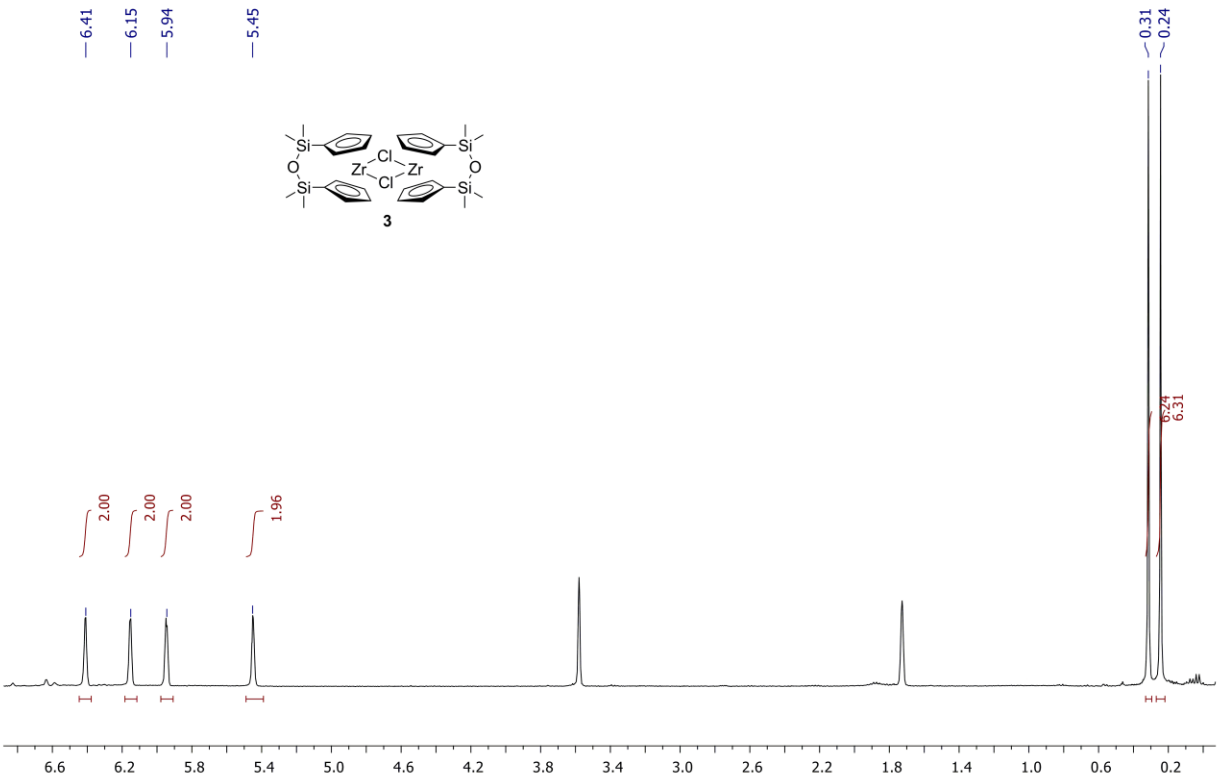


**Figure S2**. $^{1}$H NMR spectrum (THF-$d_8$, 20 °C) of {O[SiMe$_2$($\eta^5$-C$_5$H$_4$)]$_2$Zr(μ-Cl)}$_2$ (**3**).

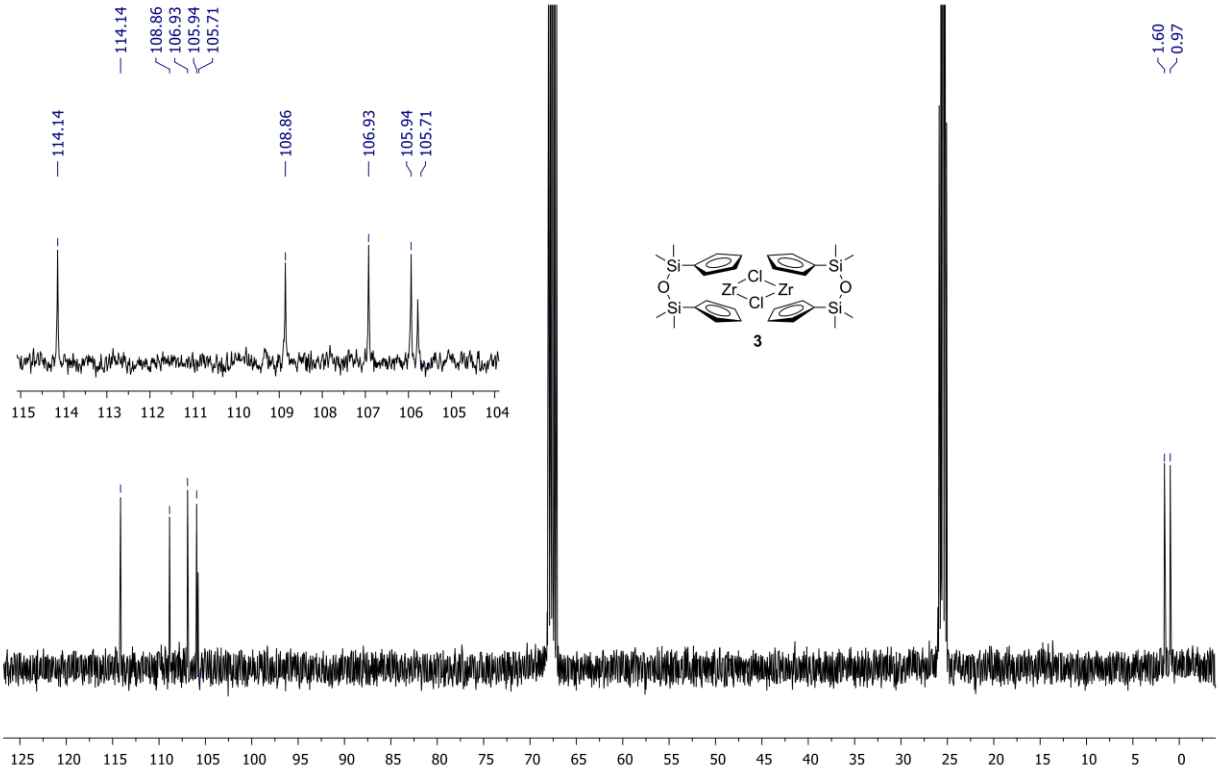


**Figure S3**. $^{13}$C NMR spectrum (THF-$d_8$, 20 °C) of {O[SiMe$_2$($\eta^5$-C$_5$H$_4$)]$_2$Zr(μ-Cl)}$_2$ (**3**).

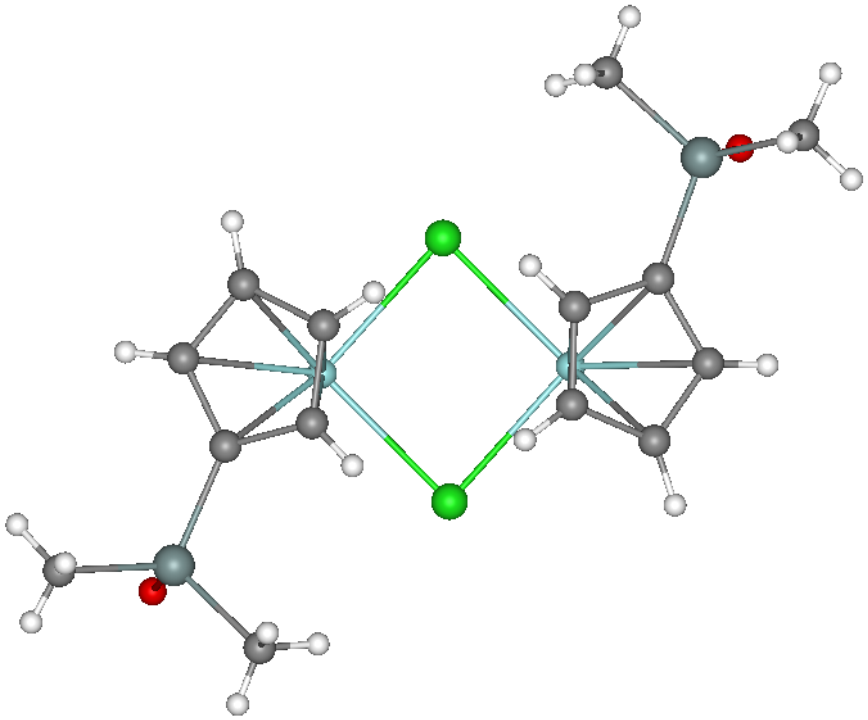

**Figure S4**. Non-equivalence of ring atoms and Me groups in {O[$SiMe_2$($\eta^5$-$C_5H_4$)]$_2$Zr(μ-Cl)}$_2$ (**3**). Two $CpSiMe_2$ fragments are omitted for clarity.

## X-ray analysis of **3**

*Crystal structure determination of **3**.* A single dark purple crystal of **3** with approximate dimensions 0.30 × 0.18 × 0.01 $mm^3$ was mounted using an inert oil in the hole of plastic CryoLoop and transferred to a cold air stream on the Bruker SMART APEX II diffractometer. Crystal data, structure solution and refinement are provided in Table S1.

**Table S1**. Crystal data, data collection, structure solution and refinement parameters for **3**.

| | |
|---|---|
| Empirical formula | $C_{28}H_{40}Cl_2O_2Si_4Zr_2$ |
| Formula weight | 774.30 |
| Color, habit | dark purple plate |
| Crystal size, mm | 0.30 × 0.18 × 0.01 |
| Crystal system, space group | Monoclinic, $P2_1/c$ |
| Unit cell dimensions: | |
| a, A | 14.6798(10) |
| b, A | 7.5088(5) |
| c, A | 15.9338(11) |
| beta, deg | 113.3880(9) |
| Volume, $A^3$ | 1612.04(19) |
| Z | 2 |
| Calculated density, g $cm^{-3}$ | 1.595 |
| Absorption coefficient, $mm^{-1}$ | 0.986 |
| F(000) | 788 |
| Temperature, K | 150(2) |
| Radiation, (λ , Å) | graphite monochromatized MoKα(0.71073) |
| Scan mode | omega |
| Step per scan, deg | 0.5 |
| Scan time, sec | 20 |
| Theta range, deg | 2.59 to 29.00 |
| Limiting indices | -20<=h<=20, -10<=k<=10, -21<=l<=21 |
| Reflections collected / unique | 17201 / 4283 [$R_{int}$ = 0.0222] |
| Completeness to theta = 29.00 | 100.0 % |
| Reflections with $I > 2\sigma(I)$ | 3791 |
| Absorption correction | Semi-empirical from equivalents |
| Min. and Max. transmission | 0.7563 and 0.9902 |
| Solution method | Direct methods |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Hydrogen treatment | All H atoms were found from difference Fourier synthesis and refined isotropically. |
| Data / restraints / parameters | 4283 / 0 / 252 |
| Goodness-of-fit on $F^2$ | 1.070 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1$ = 0.0208, w$R_2$ = 0.0512 |
| $R$ indices (all data) | $R_1$ = 0.0261, w$R_2$ = 0.0539 |
| Largest diff. peak and hole, e $A^{-3}$ | 0.521 and -0.238 |

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

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Zr(1) | 4003(1) | 6412(1) | 4343(1) | 14(1) |
| Cl(1) | 4211(1) | 2991(1) | 4468(1) | 18(1) |
| Si(1) | 1995(1) | 5227(1) | 1997(1) | 20(1) |
| Si(2) | 1320(1) | 4908(1) | 3615(1) | 19(1) |
| O(1) | 1307(1) | 5154(2) | 2591(1) | 28(1) |
| C(11) | 3192(1) | 6389(2) | 2635(1) | 17(1) |
| C(12) | 4162(1) | 5686(2) | 2851(1) | 21(1) |
| C(13) | 4874(1) | 7003(3) | 3273(1) | 25(1) |
| C(14) | 4370(1) | 8581(2) | 3327(1) | 25(1) |
| C(15) | 3346(1) | 8208(2) | 2920(1) | 20(1) |
| C(16) | 1256(2) | 6462(3) | 938(1) | 36(1) |
| C(17) | 2313(2) | 2954(3) | 1746(2) | 41(1) |
| C(21) | 2361(1) | 6214(2) | 4447(1) | 17(1) |
| C(22) | 3050(1) | 5673(2) | 5329(1) | 20(1) |
| C(23) | 3669(1) | 7106(2) | 5765(1) | 23(1) |
| C(24) | 3385(1) | 8593(2) | 5174(1) | 24(1) |
| C(25) | 2571(1) | 8050(2) | 4376(1) | 20(1) |
| C(26) | 129(1) | 5821(3) | 3574(1) | 33(1) |
| C(27) | 1452(2) | 2534(3) | 3952(2) | 37(1) |

**Table S3.** Bond lengths [Å] for **3**.

| | | | | | |
|---|---|---|---|---|---|
| Zr(1)-C(25) | 2.4543(15) | Si(2)-O(1) | 1.6358(12) | C(17)-H(172) | 0.87(3) |
| Zr(1)-C(15) | 2.4796(15) | Si(2)-C(27) | 1.849(2) | C(17)-H(173) | 1.03(3) |
| Zr(1)-C(21) | 2.4862(15) | Si(2)-C(26) | 1.8536(19) | C(21)-C(22) | 1.426(2) |
| Zr(1)-C(24) | 2.4930(15) | Si(2)-C(21) | 1.8565(16) | C(21)-C(25) | 1.427(2) |
| Zr(1)-C(11) | 2.4993(14) | C(11)-C(12) | 1.426(2) | C(22)-C(23) | 1.402(2) |
| Zr(1)-C(14) | 2.5010(16) | C(11)-C(15) | 1.429(2) | C(22)-H(22) | 0.914(18) |
| Zr(1)-C(12) | 2.5373(15) | C(12)-C(13) | 1.402(2) | C(23)-C(24) | 1.413(2) |
| Zr(1)-C(13) | 2.5412(15) | C(12)-H(12) | 0.894(19) | C(23)-H(23) | 0.91(2) |
| Zr(1)-C(22) | 2.5469(14) | C(13)-C(14) | 1.416(3) | C(24)-C(25) | 1.416(2) |
| Zr(1)-C(23) | 2.5562(15) | C(13)-H(13) | 0.92(2) | C(24)-H(24) | 0.96(2) |
| Zr(1)-Cl(1) | 2.5852(4) | C(14)-C(15) | 1.409(2) | C(25)-H(25) | 0.913(19) |
| Zr(1)-Cl(1)#1 | 2.5921(4) | C(14)-H(14) | 0.92(2) | C(26)-H(261) | 0.94(3) |
| Zr(1)-Zr(1)#1 | 3.5470(3) | C(15)-H(15) | 0.90(2) | C(26)-H(262) | 0.97(2) |
| Si(1)-O(1) | 1.6368(12) | C(16)-H(161) | 0.97(3) | C(26)-H(263) | 0.92(2) |
| Si(1)-C(16) | 1.852(2) | C(16)-H(162) | 0.86(3) | C(27)-H(271) | 0.94(3) |
| Si(1)-C(17) | 1.854(2) | C(16)-H(163) | 0.95(3) | C(27)-H(272) | 1.00(3) |
| Si(1)-C(11) | 1.8613(16) | C(17)-H(171) | 0.94(3) | C(27)-H(273) | 0.87(3) |

**Table S4.** Bond angles [deg] for **3**.

| | | | |
|---|---|---|---|
| C(25)-Zr(1)-C(15) | 73.82(5) | C(21)-Zr(1)-Cl(1) | 91.32(3) |
| C(25)-Zr(1)-C(21) | 33.58(5) | C(24)-Zr(1)-Cl(1) | 131.93(4) |
| C(15)-Zr(1)-C(21) | 93.33(5) | C(11)-Zr(1)-Cl(1) | 93.89(3) |
| C(25)-Zr(1)-C(24) | 33.25(5) | C(14)-Zr(1)-Cl(1) | 130.39(4) |
| C(15)-Zr(1)-C(24) | 92.11(6) | C(12)-Zr(1)-Cl(1) | 78.88(4) |
| C(21)-Zr(1)-C(24) | 55.69(5) | C(13)-Zr(1)-Cl(1) | 98.63(4) |
| C(25)-Zr(1)-C(11) | 89.14(5) | C(22)-Zr(1)-Cl(1) | 79.20(4) |
| C(15)-Zr(1)-C(11) | 33.35(5) | C(23)-Zr(1)-Cl(1) | 101.09(4) |
| C(21)-Zr(1)-C(11) | 90.98(5) | C(25)-Zr(1)-Cl(1)#1 | 121.58(4) |
| C(24)-Zr(1)-C(11) | 117.80(5) | C(15)-Zr(1)-Cl(1)#1 | 119.20(4) |
| C(25)-Zr(1)-C(14) | 95.39(6) | C(21)-Zr(1)-Cl(1)#1 | 133.41(4) |
| C(15)-Zr(1)-C(14) | 32.86(5) | C(24)-Zr(1)-Cl(1)#1 | 88.49(4) |
| C(21)-Zr(1)-C(14) | 123.10(5) | C(11)-Zr(1)-Cl(1)#1 | 134.72(3) |
| C(24)-Zr(1)-C(14) | 97.68(6) | C(14)-Zr(1)-Cl(1)#1 | 86.89(4) |
| C(11)-Zr(1)-C(14) | 55.39(5) | C(12)-Zr(1)-Cl(1)#1 | 106.27(4) |
| C(25)-Zr(1)-C(12) | 121.70(5) | C(13)-Zr(1)-Cl(1)#1 | 80.13(4) |
| C(15)-Zr(1)-C(12) | 53.69(5) | C(22)-Zr(1)-Cl(1)#1 | 103.31(4) |
| C(21)-Zr(1)-C(12) | 120.12(5) | C(23)-Zr(1)-Cl(1)#1 | 79.10(4) |
| C(24)-Zr(1)-C(12) | 145.78(5) | Cl(1)-Zr(1)-Cl(1)#1 | 93.514(12) |
| C(11)-Zr(1)-C(12) | 32.88(5) | C(25)-Zr(1)-Zr(1)#1 | 143.10(4) |
| C(14)-Zr(1)-C(12) | 53.86(6) | C(15)-Zr(1)-Zr(1)#1 | 142.70(4) |
| C(25)-Zr(1)-C(13) | 126.13(6) | C(21)-Zr(1)-Zr(1)#1 | 121.26(3) |
| C(15)-Zr(1)-C(13) | 53.78(5) | C(24)-Zr(1)-Zr(1)#1 | 117.89(4) |
| C(21)-Zr(1)-C(13) | 144.51(5) | C(11)-Zr(1)-Zr(1)#1 | 124.31(3) |
| C(24)-Zr(1)-C(13) | 128.86(6) | C(14)-Zr(1)-Zr(1)#1 | 115.63(4) |
| C(11)-Zr(1)-C(13) | 54.59(5) | C(12)-Zr(1)-Zr(1)#1 | 93.68(4) |
| C(14)-Zr(1)-C(13) | 32.62(6) | C(13)-Zr(1)-Zr(1)#1 | 89.09(4) |
| C(12)-Zr(1)-C(13) | 32.04(6) | C(22)-Zr(1)-Zr(1)#1 | 91.81(4) |
| C(25)-Zr(1)-C(22) | 53.88(5) | C(23)-Zr(1)-Zr(1)#1 | 90.11(4) |
| C(15)-Zr(1)-C(22) | 124.95(5) | Cl(1)-Zr(1)-Zr(1)#1 | 46.838(8) |
| C(21)-Zr(1)-C(22) | 32.89(5) | Cl(1)#1-Zr(1)-Zr(1)#1 | 46.675(9) |
| C(24)-Zr(1)-C(22) | 53.83(5) | Zr(1)-Cl(1)-Zr(1)#1 | 86.486(12) |
| C(11)-Zr(1)-C(22) | 121.96(5) | O(1)-Si(1)-C(16) | 105.68(8) |
| C(14)-Zr(1)-C(22) | 148.63(6) | O(1)-Si(1)-C(17) | 111.06(9) |
| C(12)-Zr(1)-C(22) | 143.95(5) | C(16)-Si(1)-C(17) | 111.79(12) |
| C(13)-Zr(1)-C(22) | 175.98(5) | O(1)-Si(1)-C(11) | 111.42(6) |
| C(25)-Zr(1)-C(23) | 53.91(5) | C(16)-Si(1)-C(11) | 110.37(9) |
| C(15)-Zr(1)-C(23) | 123.88(5) | C(17)-Si(1)-C(11) | 106.60(9) |
| C(21)-Zr(1)-C(23) | 54.54(5) | O(1)-Si(2)-C(27) | 110.88(9) |
| C(24)-Zr(1)-C(23) | 32.46(6) | O(1)-Si(2)-C(26) | 106.58(8) |
| C(11)-Zr(1)-C(23) | 142.21(5) | C(27)-Si(2)-C(26) | 110.86(10) |
| C(14)-Zr(1)-C(23) | 127.42(6) | O(1)-Si(2)-C(21) | 109.46(6) |
| C(12)-Zr(1)-C(23) | 174.63(5) | C(27)-Si(2)-C(21) | 109.86(9) |
| C(13)-Zr(1)-C(23) | 152.06(6) | C(26)-Si(2)-C(21) | 109.13(8) |
| C(22)-Zr(1)-C(23) | 31.88(5) | Si(2)-O(1)-Si(1) | 144.66(9) |
| C(25)-Zr(1)-Cl(1) | 124.90(4) | C(12)-C(11)-C(15) | 105.10(14) |
| C(15)-Zr(1)-Cl(1) | 127.02(4) | C(12)-C(11)-Si(1) | 126.42(12) |

| | |
|---|---|
| C(15)-C(11)-Si(1) | 128.13(12) |
| C(12)-C(11)-Zr(1) | 75.03(8) |
| C(15)-C(11)-Zr(1) | 72.57(8) |
| Si(1)-C(11)-Zr(1) | 122.47(7) |
| C(13)-C(12)-C(11) | 109.70(15) |
| C(13)-C(12)-Zr(1) | 74.13(9) |
| C(11)-C(12)-Zr(1) | 72.10(8) |
| C(13)-C(12)-H(12) | 126.8(12) |
| C(11)-C(12)-H(12) | 123.5(12) |
| Zr(1)-C(12)-H(12) | 119.1(12) |
| C(12)-C(13)-C(14) | 108.17(15) |
| C(12)-C(13)-Zr(1) | 73.83(9) |
| C(14)-C(13)-Zr(1) | 72.13(9) |
| C(12)-C(13)-H(13) | 127.3(13) |
| C(14)-C(13)-H(13) | 124.6(13) |
| Zr(1)-C(13)-H(13) | 119.1(13) |
| C(15)-C(14)-C(13) | 107.03(15) |
| C(15)-C(14)-Zr(1) | 72.74(9) |
| C(13)-C(14)-Zr(1) | 75.25(9) |
| C(15)-C(14)-H(14) | 125.6(14) |
| C(13)-C(14)-H(14) | 127.4(14) |
| Zr(1)-C(14)-H(14) | 117.7(14) |
| C(14)-C(15)-C(11) | 109.96(14) |
| C(14)-C(15)-Zr(1) | 74.40(9) |
| C(11)-C(15)-Zr(1) | 74.08(8) |
| C(14)-C(15)-H(15) | 125.7(13) |
| C(11)-C(15)-H(15) | 124.2(13) |
| Zr(1)-C(15)-H(15) | 120.8(12) |
| Si(1)-C(16)-H(161) | 109.8(16) |
| Si(1)-C(16)-H(162) | 110.6(17) |
| H(161)-C(16)-H(162) | 103(2) |
| Si(1)-C(16)-H(163) | 111.8(16) |
| H(161)-C(16)-H(163) | 112(2) |
| H(162)-C(16)-H(163) | 110(2) |
| Si(1)-C(17)-H(171) | 111.9(18) |
| Si(1)-C(17)-H(172) | 109.6(17) |
| H(171)-C(17)-H(172) | 110(2) |
| Si(1)-C(17)-H(173) | 109.5(14) |
| H(171)-C(17)-H(173) | 109(2) |
| H(172)-C(17)-H(173) | 106(2) |
| C(22)-C(21)-C(25) | 105.23(13) |
| C(22)-C(21)-Si(2) | 127.89(12) |
| C(25)-C(21)-Si(2) | 126.56(12) |
| C(22)-C(21)-Zr(1) | 75.89(8) |
| C(25)-C(21)-Zr(1) | 71.99(8) |
| Si(2)-C(21)-Zr(1) | 121.96(7) |
| C(23)-C(22)-C(21) | 109.63(14) |
| C(23)-C(22)-Zr(1) | 74.43(9) |
| C(21)-C(22)-Zr(1) | 71.21(8) |
| C(23)-C(22)-H(22) | 126.9(12) |
| C(21)-C(22)-H(22) | 123.5(12) |
| Zr(1)-C(22)-H(22) | 120.3(11) |
| C(22)-C(23)-C(24) | 108.36(15) |
| C(22)-C(23)-Zr(1) | 73.69(8) |
| C(24)-C(23)-Zr(1) | 71.31(9) |
| C(22)-C(23)-H(23) | 126.6(14) |
| C(24)-C(23)-H(23) | 125.0(14) |
| Zr(1)-C(23)-H(23) | 119.4(13) |
| C(23)-C(24)-C(25) | 106.96(14) |
| C(23)-C(24)-Zr(1) | 76.23(9) |
| C(25)-C(24)-Zr(1) | 71.88(9) |
| C(23)-C(24)-H(24) | 128.5(13) |
| C(25)-C(24)-H(24) | 124.4(13) |
| Zr(1)-C(24)-H(24) | 120.9(13) |
| C(24)-C(25)-C(21) | 109.77(14) |
| C(24)-C(25)-Zr(1) | 74.88(9) |
| C(21)-C(25)-Zr(1) | 74.43(8) |
| C(24)-C(25)-H(25) | 126.6(12) |
| C(21)-C(25)-H(25) | 123.5(12) |
| Zr(1)-C(25)-H(25) | 120.6(12) |
| Si(2)-C(26)-H(261) | 112.5(16) |
| Si(2)-C(26)-H(262) | 111.7(14) |
| H(261)-C(26)-H(262) | 107(2) |
| Si(2)-C(26)-H(263) | 111.6(14) |
| H(261)-C(26)-H(263) | 103(2) |
| H(262)-C(26)-H(263) | 110(2) |
| Si(2)-C(27)-H(271) | 109.3(19) |
| Si(2)-C(27)-H(272) | 111.9(15) |
| H(271)-C(27)-H(272) | 109(2) |
| Si(2)-C(27)-H(273) | 108.3(17) |
| H(271)-C(27)-H(273) | 114(2) |
| H(272)-C(27)-H(273) | 104(2) |

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+3/2

**Table S5.** Anisotropic displacement parameters ($Å^2$ x $10^3$) for **3**. 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) | 16(1) | 16(1) | 12(1) | 0(1) | 7(1) | -1(1) |
| Cl(1) | 19(1) | 18(1) | 17(1) | -1(1) | 7(1) | -2(1) |
| Si(1) | 20(1) | 27(1) | 16(1) | -4(1) | 9(1) | 4(1) |
| Si(2) | 18(1) | 23(1) | 19(1) | 0(1) | 10(1) | -2(1) |
| O(1) | 25(1) | 43(1) | 20(1) | -5(1) | 12(1) | -10(1) |
| C(11) | 20(1) | 21(1) | 12(1) | 2(1) | 8(1) | 0(1) |
| C(12) | 25(1) | 27(1) | 13(1) | 4(1) | 12(1) | 4(1) |
| C(13) | 18(1) | 43(1) | 16(1) | 7(1) | 8(1) | -1(1) |
| C(14) | 28(1) | 26(1) | 19(1) | 4(1) | 9(1) | -9(1) |
| C(15) | 24(1) | 20(1) | 16(1) | 5(1) | 8(1) | 1(1) |
| C(16) | 24(1) | 60(1) | 22(1) | 5(1) | 7(1) | -1(1) |
| C(17) | 39(1) | 31(1) | 55(1) | -18(1) | 22(1) | -9(1) |
| C(21) | 18(1) | 20(1) | 17(1) | 0(1) | 10(1) | 1(1) |
| C(22) | 22(1) | 25(1) | 19(1) | 3(1) | 13(1) | 3(1) |
| C(23) | 21(1) | 37(1) | 14(1) | -4(1) | 9(1) | 2(1) |
| C(24) | 25(1) | 24(1) | 26(1) | -8(1) | 13(1) | -1(1) |
| C(25) | 21(1) | 20(1) | 20(1) | 0(1) | 11(1) | 4(1) |
| C(26) | 23(1) | 48(1) | 30(1) | 1(1) | 12(1) | 3(1) |
| C(27) | 34(1) | 26(1) | 44(1) | 3(1) | 9(1) | -7(1) |

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

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(12) | 4277(14) | 4560(30) | 2738(13) | 23(5) |
| H(13) | 5551(16) | 6890(30) | 3492(14) | 31(5) |
| H(14) | 4648(17) | 9660(30) | 3575(15) | 38(6) |
| H(15) | 2855(15) | 9000(30) | 2823(13) | 23(5) |
| H(22) | 3071(13) | 4550(20) | 5555(12) | 18(4) |
| H(23) | 4181(16) | 7090(30) | 6324(14) | 35(6) |
| H(24) | 3642(16) | 9790(30) | 5287(15) | 31(5) |
| H(25) | 2197(14) | 8760(20) | 3897(13) | 20(5) |
| H(161) | 1134(19) | 7660(40) | 1089(18) | 60(8) |
| H(162) | 670(20) | 6030(40) | 685(17) | 54(7) |
| H(163) | 1560(20) | 6460(30) | 517(18) | 57(8) |
| H(171) | 2700(20) | 2340(40) | 2280(20) | 68(9) |
| H(172) | 1770(20) | 2370(40) | 1444(17) | 55(7) |
| H(173) | 2694(19) | 3040(30) | 1327(17) | 55(7) |
| H(261) | 57(19) | 7040(40) | 3431(17) | 57(8) |
| H(262) | -439(19) | 5210(30) | 3118(17) | 47(7) |
| H(263) | 94(16) | 5770(30) | 4136(16) | 38(6) |
| H(271) | 2060(20) | 2100(40) | 3970(20) | 75(9) |
| H(272) | 1420(20) | 2350(40) | 4564(19) | 63(8) |
| H(273) | 935(19) | 1970(30) | 3580(17) | 48(7) |

## Hex-1-ene oligomerization experiments

*Typical procedure for determining the catalytic activity in 1-hexene dimerization*

Hex-1-ene (25 ml, 200 mmol) and a 1 *M* $Bu^i_3Al$ solution in hexane (2 ml, 20 mmol) were mixed in a two-necked flask prefilled with argon, which was then placed in a thermostated bath with diethylene glycol. After maintaining the external bath at 60 °C for 5 min, a solution or suspension of $LZrCl_2$ precatalyst (0.1 mmol) in toluene (6 ml) was added. After 20 min of stirring, a 1.5 *M* MeAlO solution (0.66 ml, 1 mmol) was added. The sampling was performed after 1, 2, 5, 10, 15, 20 and 30 min, oligomer composition was analyzed by GC.