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Highly selective propylene dimerization catalyzed by C_1-symmetric zirconocene complexes

Wenzhong Huang, Yan Wang, Haiyan Ma* and Jiling Huang*

A series of ethylene-bridged C_1-symmetric *ansa*-(3-*R*-indenyl)(fluorenyl) zirconocene complexes (1–9) incorporating a pendant arene substituent on the 3-position of indenyl ring have been synthesized. The structure of complex 4 was further confirmed by X-ray diffraction analysis. When activated with methylaluminoxane, four sterically less encumbered complexes 1, 2, 4 and 5 could catalyze the dimerization of propylene in toluene at 100°C to afford 2-methyl-1-pentene with high selectivities up to 95.7–98.4% and moderate activities of 2.00×10^4 to 7.89×10^4 g (mol-Zr·h)$^{-1}$. Copyright © 2014 John Wiley & Sons, Ltd.

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Introduction

The products of propylene dimerization, such as 2-methyl-1-pentene and 4-methyl-1-pentene, are important olefin oligomers and are widely used to synthesize economically valued products, e.g. drugs[1] and branched polymers.[2] Typically, 2-methyl-1-pentene is effectively produced (>90% in all products) at extremely high temperature and pressure with catalyst systems based on alkylaluminum.[3] Considering the risk of the process, many efforts have been devoted to the single-site transition metal catalysts, such as nickel,[4] cobalt,[5] iron[6] or vanadium[7] complexes with bis(imino)pyridine,[7,8] diimine[9] or phosphorus-based[10] chelating ligands, which are capable of catalyzing propylene dimerization under mild conditions. Unfortunately, as described in the literature, these complexes exhibit low selectivity towards a specific dimer, in most cases giving a mixture of hexenes, methyl pentenes and dimethyl butenes.[4–10]

Group IV metallocene complexes are well-known catalysts for propylene polymerization,[11] and by modifying the ligands' skeleton or changing the polymerization conditions the microstructures of polymer chains can be conveniently tuned. In contrast, there are only rare examples of metallocene complexes reported for propylene oligomerization or dimerization.[12] Kaminsky[13] reported that, at an extremely low monomer feed rate, ethylene-bis(tetrahydroindenyl) zirconium dichloride could dimerize propylene to 2-methyl-1-pentene with a selectivity of 99.8% in all dimeric products. However, due to the quite low activity, the reaction time had to be expanded to 15–24 h and no activity data were reported. Okuda and co-workers[14] described a series of unbridged hafnocene complexes, e.g. $(^t BuC_5Me_4)_2HfCl_2$, which showed moderate activity for propylene oligomerization with the percentage of 4-methyl-1-pentene up to 61.6% in all products, indicating the crucial role of the bulky substituent on the Cp′ ring for propylene dimerization. Herein we report a series of ethylene-bridged C_1-symmetric *ansa*-(3-*R*-indenyl)(fluorenyl) zirconocene complexes that incorporate a pendant arene substituent on the 3-position of indenyl ring. Upon activation with methylaluminoxane (MAO), these complexes display moderate activity and high selectivity for propylene dimerization, with 2-methyl-1-pentene almost as the only product.

Experimental

General Procedures

All manipulations were carried out under a dry argon atmosphere using standard Schlenk techniques unless otherwise indicated. THF, diethyl ether (Et_2O), *n*-hexane, petroleum ether (30–60°C) and toluene were distilled from sodium–benzophenone prior to use. Dichloromethane (CH_2Cl_2) was distilled from calcium hydride under argon. Chloroform-*d* was dried over calcium hydride under argon and stored in the presence of activated 4 Å molecular sieves. *n*-BuLi (in *n*-hexane) was purchased from Acros. MAO (1.53 M in toluene) was purchased from Witco GmbH. Polymer-grade ethylene was directly used for polymerization. 9-(2-Bromoethyl)-fluorene[15] and 6,6-dimethylbenzofulvene[16] were prepared according to literature procedures. ^{13}C (100 MHz) and ^1H (400 MHz) NMR measurements were obtained in $CDCl_3$ solution on a Bruker Avance 400 spectrometer. Chemical shifts for NMR spectra were referenced internally using the residual solvent resonances and reported relative to TMS. Elemental analyses for C, N and H were carried out on an Elementar III Vario EI analyzer. The products of propylene oligomerization were characterized by a GC-MS instrument (Focus DSQ™, Thermo Scientific).

* *Correspondence to: Jiling Huan and Haiyan Ma, Laboratory of Organometallic Chemistry, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, People's Republic of China. E-mail: jlhuang@ecust.edu.cn; haiyanma@ecust.edu.cn*

Laboratory of Organometallic Chemistry, East China University of Science and Technology, Shanghai, 200237, People's Republic of China

High-resolution mass spectra were performed on a Micromass Q-TOF Micro mass spectrometer with an ESI source (Waters, Manchester, UK).

Synthesis of Proligands

*1-(9-Fluorenyl)-2-{1-[3-(2-(2-phenylpropyl))indenyl]}ethane (**L^1H_2**)*

A solution of *n*-BuLi in *n*-hexane (36.0 ml, 2.30 mol l^{-1}, 83.0 mmol) at 0°C was added dropwise to a solution of bromobenzene (8.0 ml, 76 mmol) in 30 ml dry Et_2O. The reaction mixture was stirred overnight at room temperature (r.t.) and then 6,6-dimethylbenzofulvene (9.08 g, 58.0 mmol) was added dropwise. After stirring overnight at r.t., the reaction mixture was quenched with 50 ml aqueous ammonium chloride. The organic phase was separated and the aqueous layer was extracted with Et_2O. The combined organic phases were dried over anhydrous $MgSO_4$. After filtration, the solvents were removed under vacuum. The product of 3-[2-(2-phenylpropyl)]indene (**Ind 1**) was isolated via distillation under reduced pressure as a yellow oil (128–132°C/40 Pa, 8.3 g, 82%). This compound was analyzed by ^{1}H NMR spectroscopy and was used without further purification.

To a solution of **Ind 1** (3.46 g, 14.8 mmol) in 30 ml dry Et_2O at 0°C was added dropwise a solution of *n*-BuLi (7.0 ml, 2.15 mol l^{-1}, 15 mmol) in *n*-hexane. The solution was stirred at r.t. for 5 h and then added via cannula to a solution of 9-(2-bromoethyl)-fluorene (3.46 g, 12.7 mmol) in 20 ml of dry Et_2O. The reaction mixture was stirred overnight at r.t. and then quenched with 50 ml aqueous NH_4Cl. The organic phase was separated and the aqueous layer was extracted with Et_2O. The combined organic phases were dried ($MgSO_4$) and filtered, and the filtrate was concentrated under vacuum. The resulting light-yellow oil was dissolved in petroleum ether and kept at −20°C to afford an off-white solid (4.40 g, 81.6%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 7.72 (d, J = 7.6 Hz, 2H, 4,5-Flu-*H*), 7.48 (d, J = 7.6 Hz, 1H, 1-Flu-*H*), 7.41 (d, J = 7.6 Hz, 1H, 8-Flu-*H*), 7.34-7.32 (m, 2H, 3,5-Ph-*H*), 7.30–7.26 (m, 4H, 2,6-Ph—*H*, 2,7-Flu—*H*), 7.23–7.18 (m, 3H, 4-Ph—*H*, 3,6-Flu—*H*), 7.13 (d, J = 6.8 Hz, 1H, 7-Ind—*H*), 7.00–6.92 (m, 2H, 5,6-Ind—*H*), 6.61 (d, J = 7.6 Hz, 1H, 4-Ind—*H*), 6.33 (d, J = 2.0 Hz, 1H, 2-Ind—C*H*), 3.96 (t, J = 5.4 Hz, 1H, 9-Flu—*CH*), 3.35 (t, J = 5.6 Hz, 1H, 1-Ind—*CH*), 2.19–2.10 (m, 1H, CH_2CH_2), 1.99–1.90 (m, 1H, CH_2CH_2), 1.78–1.69 (m, 1H, CH_2CH_2), 1.63 (s, 3H, CH_3), 1.62 (s, 3H, CH_3), 1.45–1.36 (m, 1H, CH_2CH_2). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ 151.5 (1-Ph—*C*), 148.7 (7a-Ind—*C*), 147.9 (3a-Ind—*C*), 147.0 and 146.9 (8a,9a-Flu—*C*), 143.3 (3-Ind—*C*), 141.22 and 141.20 (4a,4b-Flu—*C*), 132.1 (2-Ind—*C*), 128.2 (3,5-Ph—*C*), 126.9 (3,6-Flu—*C*), 126.8 (2,7-Flu—*C*), 126.1 (2,6-Ph—*C*), 125.73 (4-Ph—*C*), 125.66 (5-Ind—*C*), 124.3 (4,5-Flu—*C*), 124.1 (6-Ind—*C*), 122.7 (4-Ind—*C*), 122.3 (7-Ind—*C*), 119.81 and 119.77 (1,8-Flu—*C*), 48.0 (1-Ind—CH_2), 47.4 (9-Flu—CH), 40.3 ($C(CH_3)_2$), 30.0 ($C(CH_3)_2$), 29.3 (CH_2CH_2), 29.2 ($C(CH_3)_2$), 26.9 (CH_2CH_2).

*1-(9-Fluorenyl)-2-{1-[3-(2-(2-phenylpentyl))indenyl]}ethane (**L^2H_2**)*

Following the procedure described above, *n*-BuLi (35.0 ml, 2.39 mol l^{-1}, 84.0 mmol), bromobenzene (8.0 ml, 76 mmol) and 6-methyl-6-propylbenzofulvene (9.97 g, 54.0 mmol) were used. The product of 3-[2-(2-phenylpentyl)]indene (**Ind 2**) was isolated via distillation under reduced pressure as a yellow oil (56–60°C/15 Pa, 7.30 g, 51.2%). This compound was analyzed by ^{1}H NMR spectroscopy and was used without further purification.

A yellow solid was produced analogously to **L^1H_2** in 37.1% yield (1.35 g) from **Ind 2** (2.10 g, 8.00 mmol), *n*-BuLi (4.50 ml, 1.79 mol l^{-1}, 8.00 mmol) and 9-(2-bromoethyl)- fluorene (2.17 g, 8.0 mmol). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 7.78 (d, J = 7.6 Hz, 2H, 4,5-Flu—*H*), 7.54 (d, J = 7.3 Hz, 1H, 1-Flu—*H*), 7.45 (d, J = 7.4 Hz, 1H, 8-Flu—*H*), 7.41–7.30 (m, 4H, 3,5-Ph—*H*, 2,7-Flu—*H*), 7.29–7.20 (m, 5H, 2,4,6-Ph—*H*, 3,6-Flu—*H*), 7.17–7.14 (m, 1H, 7-Ind—*H*), 7.04 (dt, J = 7.4, 0.7 Hz, 0.7H, 6-Ind—*H*), 7.02 (dt, J = 7.4, 0.7 Hz, 0.3H, 6-Ind—*H*), 6.94 (t, J = 7.4 Hz, 0.7H, 5-Ind—*H*), 6.93 (t, J = 7.4 Hz, 0.3H, 5-Ind—*H*), 6.61 (d, J = 7.6 Hz, 0.7H, 7-Ind—*H*), 6.59 (d, J = 7.6 Hz, 0.3H, 7-Ind—*H*), 6.38 (d, J = 1.9 Hz, 0.3H, 2-Ind—C*H*), 6.36 (d, J = 1.9 Hz, 0.7H, 2-Ind—C*H*), 4.01 (t, J = 5.4 Hz, 1H, 9-Flu—C*H*), 3.42–3.38 (m, 1H, 1-Ind—CH_2), 2.23–2.09 (m, 2H, IndCH_2CH_2Flu, $CH_2CH_2CH_3$), 2.02–1.92 (m, 2H, IndCH_2CH_2Flu, $CH_2CH_2CH_3$), 1.84–1.73 (m, 1H, IndCH_2CH_2Flu), 1.61 (s, 2.1H, CCH_3), 1.55 (s, 0.9H, CCH_3), 1.48–1.39 (m, 1H, IndCH_2CH_2Flu), 1.18–1.04 (m, 2H, $CH_2CH_2CH_3$), 0.89–0.84 (m, 3H, $CH_2CH_2CH_3$). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ 150.3 (1-Ph—*C*), 148.6 (7a-Ind—*C*), 147.4 (3a-Ind—*C*), 147.01 and 146.95 (8a,9a-Flu—*C*), 143.5 (3-Ind—*C*), 141.23 and 141.20 (4a,4b-Flu—*C*), 133.2 (2-Ind—*C*), 128.1 (3,5-Ph—*C*), 127.0 (3,6-Flu—*C*), 126.8 (2,7-Flu—*C*), 126.6 (2,6-Ph—*C*), 125.7 (4-Ph—*C*), 125.6 (5-Ind—*C*), 124.30 and 124.27 (4,5-Flu—*C*), 124.0 (6-Ind—*C*), 122.6 (4-Ind—*C*), 122.2 (7-Ind—*C*), 119.83 and 119.79 (1,8-Flu—*C*), 48.0 (1-Ind—CH_2), 47.4 (9-Flu—*CH*), 43.6 (CH_2CCH_3), 42.5 ($CH_2CH_2CH_3$), 29.2 ($PhCH_2CH_2$), 26.9 ($PhCH_2CH_2$), 26.8 (CCH_3), 17.7 ($CH_2CH_2CH_3$), 14.8 ($CH_2CH_2CH_3$).

*1-(9-Fluorenyl)-2-{1-[3-(3-(3-phenylpentyl))indenyl]}ethane (**L^3H_2**)*

Following the procedure described above, *n*-BuLi (43.6 ml, 2.39 mol l^{-1}, 104 mmol), bromobenzene (10.0 ml, 95 mmol) and 6,6-diethylbenzofulvene (13.1 g, 71.0 mmol) were used. The product of 3-[3-(3-phenylpentyl)]indene (**Ind 3**) was isolated via distillation under reduced pressure as a yellow oil (106–110°C/40 Pa, 11.04 g, 59.0%). This compound was analyzed by ^{1}H NMR spectroscopy and was used without further purification.

A yellow solid was produced analogously to **L^1H_2** in 79.3% yield (1.90 g) from **Ind 3** (1.74 g, 6.63 mmol), *n*-BuLi (2.80 mL, 2.39 mol l^{-1}, 6.69 mmol) and 9-(2-bromoethyl)- fluorene (1.44 g, 5.27 mmol). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 7.78–7.75 (m, 2H, 4,5-Flu—*H*), 7.54 (d, J = 7.4 Hz, 1H, 1-Flu—*H*), 7.44 (d, J = 7.2 Hz, 1H, 8-Flu—*H*), 7.40–7.29 (m, 4H, 3,5-Ph—*H*, 2,7-Flu—*H*), 7.28–7.21 (m, 4H, 2,6-Ph—*H*, 3,6-Flu—*H*), 7.19 (d, J = 7.4 Hz, 1H, 7-Ind—*H*), 7.16–7.14 (m, 1H, 4-Ph—*H*), 7.01 (m, 1H, 5-Ind—*H*), 6.89 (t, J = 7.4 Hz, 1H, 6-Ind—*H*), 6.53 (d, J = 7.7 Hz, 1H, 4-Ind—*H*), 6.42 (d, J = 1.9 Hz, 1H, 2-Ind—C*H*), 4.02 (t, J = 5.4 Hz, 1H, 9-Flu—C*H*), 3.43-3.39 (m, 1H, 1-Ind—CH_2), 2.26–2.11 (m, 3H, CH_2CH_3, CH_2CH_2), 2.09–1.94 (m, 3H, CH_2CH_3, CH_2CH_2), 1.82–1.73 (m, 1H, CH_2CH_2), 1.44–1.34 (m, 1H, CH_2CH_2), 0.68 (t, J = 7.4 Hz, 3H, CH_2CH_3), 0.65 (t, J = 7.4 Hz, 3H, CH_2CH_3). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ 148.7 (7a-Ind—*C*), 147.5 (3a-Ind—*C*), 147.0 and 146.9 (8a,9a-Flu—*C*), 145.9 (1-Ph—*C*), 143.5 (3-Ind—*C*), 141.24 and 141.21 (4a,4b-Flu—*C*), 134.6 (2-Ind—*C*), 127.9 (3,5-Ph—*C*), 127.4 (3,6-Flu—*C*), 126.93 and 126.92 (2,7-Flu—*C*), 126.8 (2,6-Ph—*C*), 125.7 (4-Ph—*C*), 125.5 (5-Ind—*C*), 124.2 (4,5-Flu—*C*), 124.0 (6-Ind—*C*), 122.5 (4-Ind—*C*), 122.2 (7-Ind—*C*), 119.83 and 119.77 (1,8-Flu—*C*), 48.1 (1-Ind—CH_2), 47.3 (9-Flu—CH), 47.1 ($C(C_2H_5)$), 29.3(CH_2CH_2), 27.4 (CH_2CH_3), 27.1 (CH_2CH_3), 26.9 (CH_2CH_2), 8.4 (CH_2CH_3), 8.2 (CH_2CH_3).

*1-(9-Fluorenyl)-2-{1-[3-(2-(2-(2-methylphenyl)propyl))indenyl]}ethane (**L^4H_2**)*

Following the procedure described above, *n*-BuLi (34.8 ml, 2.39 mol l^{-1}, 83.0 mmol), *o*-bromotoluene (10.0 ml, 83 mmol) and 6,6-dimethylbenzofulvene (6.72 g, 43.0 mmol) were used. The product of 3-{2-[2-(2-methylphenyl)propyl]}indene (**Ind 4**) was isolated via distillation under reduced pressure as an orange oil

(110–114°C/10 Pa, 5.47 g, 51.2%). This compound was analyzed by ^{1}H NMR spectroscopy and was used without further purification.

A yellow solid was produced analogously to $\mathbf{L^1H_2}$ in 62.8% yield (3.04 g) from **Ind 4** (3.25 g, 13.1 mmol), *n*-BuLi (5.5 ml, 2.39 mol l^{-1}, 13.1 mmol) and 9-(2-bromoethyl)- fluorene (3.00 g, 11.1 mmol). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 7.78–7.76 (m, 2H, 4,5-Flu—*H*), 7.60 (d, J = 7.6 Hz, 1H, 3-Ph—*H*), 7.54 (d, J = 7.2 Hz, 1H, 1-Flu—*H*), 7.45 (d, J = 7.2 Hz, 1H, 8-Flu—*H*), 7.41–7.32 (m, 5H, 7-Ind-*H*, 2,3,6,7-Flu-*H*), 7.21–7.15 (m, 2H, 4,5-Ph—*H*), 7.04 (t, J = 7.4 Hz, 1H, 6-Ind—*H*), 6.97 (d, J = 7.4 Hz, 1H, 4-Ind—*H*), 6.91 (t, J = 7.4 Hz, 1H, 5-Ind—*H*), 6.48 (d, J = 7.6 Hz, 1H, 6-Ph—*H*), 6.34 (d, J = 1.6 Hz, 1H, 2-Ind—*CH*), 4.02 (t, J = 5.4 Hz, 1H, 9-Flu—*CH*), 3.34 (t, J = 5.9 Hz, 1H, 1-Ind—*CH*), 2.42–2.33 (m, 1H, CH_2CH_2), 2.28–2.17 (m, 1H, CH_2CH_2), 2.04 (s, 3H, Ph—CH_3), 1.80–1.70 (m, 1H, CH_2CH_2), 1.73 (s, 3H, CH_3), 1.70 (s, 3H, CH_3), 1.39–1.29 (m, 1H, CH_2CH_2). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ 152.2 (1-Ph—*C*), 148.6 (7a-Ind—*C*), 146.94 and 146.89 (8a,9a-Flu—*C*), 144.9 (3a-Ind—*C*), 143.5 (3-Ind—*C*), 141.23 and 141.20 (4a, 4b-Flu—*C*), 137.2 (2-Ind—*C*), 132.2 (2-Ph—*C*), 130.6 (3-Ph—*C*), 126.9 (3,6-Flu—*C*), 126.8 (2,7-Flu—*C*), 126.3 (4-Ph—*C*), 126.0 (5-Ph—*C*), 125.9 (6-Ph—*C*), 125.8 (5-Ind—*C*), 124.23 (6-Ind—*C*), 124.17 (4,5-Flu—*C*), 122.6 (4-Ind—*C*), 121.3 (7-Ind—*C*), 119.82 and 119.77 (1,8-Flu—*C*), 48.1 (1-Ind—CH_2), 47.4 (9-Flu—*CH*), 40.6 ($C(CH_3)_2$), 29.8 (CH_2CH_2), 29.4 (2C, $C(CH_3)_2$), 26.7 (CH_2CH_2), 21.4 (Ph-CH_3).

1-(9-Fluorenyl)-2-{1-[3-(2-(2-(2-methylphenyl)pentyl))indenyl]}ethane ($\mathbf{L^5H_2}$)

Following the procedure described above, *n*-BuLi (44.6 ml, 1.58 mol l^{-1}, 71.0 mmol), *o*-bromotoluene (8.0 ml, 67 mmol) and 6-methyl-6-propylbenzofulvene (6.70 g, 36.0 mmol) were used. The product of 3-{2-[2-(2-methylphenyl)pentyl]}indene (**Ind 5**) was isolated via distillation under reduced pressure as an orange oil (114–118°C/10 Pa, 6.56 g, 65.3%). This compound was analyzed by ^{1}H NMR spectroscopy and was used without further purification.

A yellow solid was produced analogously to $\mathbf{L^1H_2}$ in 61.3% yield (2.21 g) from **Ind 5** (2.13 g, 7.71 mmol), *n*-BuLi (4.30 ml, 1.79 mol l^{-1}, 7.70 mmol) and 9-(2-bromoethyl)- fluorene (2.10 g, 7.69 mmol). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 7.79–7.77 (m, 2H, 4, 5-Flu—*H*), 7.57–7.55 (m, 2H, 1,8-Flu—*H*), 7.46 (d, J = 7.1 Hz, 1H, 3-Ph—*H*), 7.43–7.32 (m, 4H, 2,3,6,7-Flu—*H*), 7.27 (m, 1H, 6-Ind—*H*), 7.22 (d, J = 7.4 Hz, 1H, 7-Ind—*H*), 7.15 (m, 1H, 5-Ph—*H*), 7.05 (m, 1H, 4-Ph—*H*), 6.97 (d, J = 7.3 Hz, 1H, 6-Ph—*H*), 6.91 (t, J = 7.2 Hz, 1H, Ph—*H*), 6.46 (d, J = 7.9 Hz, 1H, 4-Ind—*H*), 6.34 (s, 1H, 2-Ind—*CH*), 4.03 (t, J = 5.2 Hz, 1H, 9-Flu—*CH*), 3.39–3.35 (m, 1H, 1-Ind—CH_2), 2.26–2.19 (m, 2H, IndCH_2CH_2Flu, $CH_2CH_2CH_3$), 2.08–2.00 (m, 2H, IndCH_2CH_2Flu, $CH_2CH_2CH_3$), 2.03 (s, 3H, Ph—CH_3), 1.82–1.73 (m, 1H, IndCH_2CH_2Flu), 1.70 (s, 3H, CCH_3), 1.42–1.30 (m, 1H, IndCH_2CH_2Flu), 1.01–0.88 (m, 5H, $CH_2CH_2CH_3$, $CH_2CH_2CH_3$). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ 151.5 (1-Ph—*C*), 148.6 (7a-Ind—*C*), 147.0 and 146.9 (8a,9a-Flu—*C*), 143.7 (3,3a-Ind—*C*), 141.23 and 141.19 (4a,4b-Flu—*C*), 137.4 (2-Ind—*C*), 132.2 (2-Ph—*C*), 131.4 (3-Ph—*C*), 127.1 (4-Ph—*C*), 126.9 (3,6-Flu—*C*), 126.84 and 126.83 (2,7-Flu—*C*), 126.2 (5-Ph—*C*), 125.7 (6-Ph—*C*), 125.6 (5-Ind—*C*), 124.27 and 124.22 (4,5-Flu—*C*), 124.1 (6-Ind—*C*), 122.5 (4-Ind—*C*), 121.3 (7-Ind—*C*), 119.83 and 119.78 (1,8-Flu—*C*), 48.0 (1-Ind—CH_2), 47.4 (9-Flu—*CH*), 43.8 (CH_2CCH_3), 41.5 ($CH_2CH_2CH_3$), 29.7 (PhCH_2CH_2), 26.8 (PhCH_2CH_2), 26.7 (CCH_3), 21.5 (Ph—CH_3), 17.9 ($CH_2CH_2CH_3$), 14.8 ($CH_2CH_2CH_3$).

1-(9-Fluorenyl)-2-{1-[3-(3-(3-(2-methylphenyl)pentyl))indenyl]}ethane ($\mathbf{L^6H_2}$)

Following the procedure described above, *n*-BuLi (34.8 ml, 2.39 mol l^{-1}, 83.0 mmol), *o*-bromotoluene (10.0 ml, 83 mmol) and 6,6-diethylbenzofulvene (9.0 g, 49.0 mmol) were used. The product of 3-{3-[3-(2-methylphenyl)pentyl]}indene (**Ind 6**) was isolated via distillation under reduced pressure as an orange oil (114–118°C/10 Pa, 5.60 g, 41.5%). This compound was analyzed by ^{1}H NMR spectroscopy and was used without further purification.

A yellow solid was produced analogously to $\mathbf{L^1H_2}$ in 67.7% yield (1.80 g) from **Ind 6** (1.97 g, 7.13 mmol), *n*-BuLi (2.98 ml, 2.39 mol l^{-1}, 7.12 mmol) and 9-(2-bromoethyl)- fluorene (1.55 g, 5.67 mmol). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 7.77–7.75 (m, 2H, 4,5-Flu—*H*), 7.58 (d, J = 7.8 Hz, 1H, 1-Flu—*H*), 7.54 (d, J = 7.3 Hz, 1H, 8-Flu—*H*), 7.44 (d, J = 7.3 Hz, 1H, 3-Ph—*H*), 7.41–7.29 (m, 4H, 2,3,6,7-Flu—*H*), 7.24 (m, 1H, 5-Ph—*H*), 7.17 (d, J = 7.4 Hz, 1H, 7-Ind—*H*), 7.12 (dt, J = 7.4, 0.8 Hz, 1H, 6-Ind—*H*), 7.00 (dt, J = 7.4, 0.7 Hz, 1H, 5-Ind—*H*), 6.93 (d, J = 6.9 Hz, 1H, 6-Ph—*H*), 6.84 (m, 1H, 4-Ph—*H*), 6.40 (d, J = 7.7 Hz, 1H, 4-Ind—*H*), 6.35 (d, J = 2.0 Hz, 1H, 2-Ind—*CH*), 4.04 (t, J = 5.4 Hz, 1H, 9-Flu—*CH*), 3.36–3.34 (m, 1H, 1-Ind—CH_2), 2.33–2.16 (m, 3H, CH_2CH_3, CH_2CH_2), 2.13–2.03 (m, 3H, CH_2CH_3, CH_2CH_2), 1.99 (s, 3H, Ph—CH_3), 1.80–1.71 (m, 1H, CH_2CH_2), 1.32–1.25 (m, 1H, CH_2CH_2), 0.66 (t, J = 7.3 Hz, 3H, CH_2CH_3), 0.63 (t, J = 7.3 Hz, 3H, CH_2CH_3). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ 148.8 (1-Ph—*C*), 148.5 (7a-Ind—*C*), 146.93 and 146.86 (8a,9a-Flu—*C*), 143.7 (3a-Ind—*C*), 142.9 (3-Ind—*C*), 141.3 and 141.2 (4a,4b-Flu—*C*), 137.6 (2-Ind—*C*), 133.4 (2-Ph—*C*), 132.4 (3-Ph—*C*), 127.7 (4-Ph—*C*), 126.94 and 126.93 (3,6-Flu—*C*), 126.8 (2,7-Flu—*C*), 126.0 (5-Ph—*C*), 125.6 (6-Ph—*C*), 125.3 (5-Ind—*C*), 124.20 and 124.16 (4,5-Flu—*C*), 124.09 (6-Ind—*C*), 122.5 (4-Ind—*C*), 121.4 (7-Ind—*C*), 119.84 and 119.77 (1,8-Flu—*C*), 48.2 (1-Ind—CH_2), 47.4 (9-Flu—*CH*), 47.0 (*C*(C_2H_5)), 30.1 (CH_2CH_2), 26.8 (CH_2CH_2), 25.51 (CH_2CH_3), 25.47 (CH_2CH_3), 21.7 (Ph—CH_3), 8.6 (CH_2CH_3), 8.4 (CH_2CH_3).

1-(9-Fluorenyl)-2-{1-[3-(2-(2-(2-methoxyphenyl)propyl))indenyl]} ethane ($\mathbf{L^7H_2}$)

Following the procedure described above, *n*-BuLi (10.3 ml, 2.39 mol l^{-1}, 24.5 mmol), 2-bromoanisole (4.59 g, 24.5 mmol) and 6,6-dimethylbenzofulvene (3.69 g, 20.0 mmol) were used. The product of 3-{2-[2-(2-methoxyphenyl)propyl]}indene (**Ind 7**) was crystallized with diethyl ether as colorless crystalline solids (3.12 g, 59.0%) and was used without further purification.

A yellow solid was produced analogously to $\mathbf{L^1H_2}$ in 42.1% yield (1.24 g) from **Ind 7** (1.70 g, 6.43 mmol), *n*-BuLi (4.00 ml, 1.60 mol l^{-1}, 6.40 mmol) and 9-(2-bromoethyl)- fluorene (1.75 g, 6.41 mmol). This compound was analyzed by ^{1}H NMR spectroscopy and was used without further purification. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 7.78 (d, J = 7.2 Hz, 2H, 4,5-Flu—*H*), 7.54 (d, J = 7.6 Hz, 1H, 1-Flu—*H*), 7.49 (d, J = 7.4 Hz, 1H, 8-Flu—*H*), 7.43–7.37 (m, 3H, 7-Ind—*H*, 2,7-Flu—*H*), 7.33 (dt, J = 7.4, 1.2 Hz, 2H, 3,6-Flu—*H*), 7.24–7.20 (m, 2H, 6-Ind—*H*, 6-Ph—*H*), 7.04–7.02 (m, 1H, 5-Ind—*H*), 6.98–6.93 (m, 2H, 3,5-Ph—*H*), 6.76–6.75 (m, 1H, 4-Ph—*H*), 6.62 (d, J = 7.6 Hz, 1H, 4-Ind—*H*), 6.27 (d, J = 2.1 Hz, 1H, 2-Ind—*CH*), 4.03 (t, J = 5.5 Hz, 1H, 9-Flu—*CH*), 3.37 (s, 3H, OCH_3), 3.36–3.32 (m, 1H, 1-Ind—CH_2), 2.29–2.20 (m, 1H, CH_2CH_2), 2.09–2.01 (m, 1H, CH_2CH_2), 1.80–1.68 (m, 1H, CH_2CH_2), 1.72 (s, 3H, $C(CH_3)_2$), 1.71 (s, 3H, $C(CH_3)_2$), 1.43–1.35 (m, 1H, CH_2CH_2).

1-(9-Fluorenyl)-2-{1-[3-(2-(2-(2-methoxyphenyl)pentyl))indenyl]} ethane ($\mathbf{L^8H_2}$)

Following the procedure described above, *n*-BuLi (15.3 ml, 1.79 mol l^{-1}, 27.4 mmol), 2-bromoanisole (5.10 g, 27.3 mmol) and 6,6-diethylbenzofulvene (3.99 g, 21.7 mmol) were used. The product of 3-{2-[2-(2-methoxyphenyl)pentyl]}indene (**Ind 8**) was recrystallized with diethyl ether as an off-white powder (3.23 g, 51.0%). This compound was analyzed by ^{1}H NMR spectroscopy and was used without further purification.

A yellow solid was produced analogously to $\mathbf{L^1H_2}$ in 41.3% yield (1.23 g) from **Ind 8** (1.80 g, 6.16 mmol), *n*-BuLi (3.85 ml, 1.60 mol l^{-1},

6.16 mmol) and 9-(2-bromoethyl)- fluorene (1.68 g, 6.15 mmol). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 7.76 (d, J = 7.4 Hz, 2H, 4,5-Flu—*H*), 7.53 (d, J = 7.3 Hz, 1H, 1-Flu—*H*), 7.46 (d, J = 7.3 Hz, 1H, 8-Flu—*H*), 7.38–7.36 (m, 3H, 7-Ind—*H*, 2,7-Flu—*H*), 7.32–7.30 (m, 2H, 3,6-Flu—*H*), 7.20–7.18 (m, 2H, 6-Ind—*H*, 6-Ph—*H*), 7.00 (t, J = 7.3 Hz, 1H, 5-Ind—*H*), 6.95–6.94 (m, 2H, 4,5-Ph—*H*), 6.73 (d, J = 8.0 Hz, 1H, 3-Ph—*H*), 6.56 (d, J = 7.6 Hz, 1H, 4-Ind—*H*), 6.22 (d, J = 1.3 Hz, 1H, 2-Ind—C*H*), 4.01 (t, J = 5.4 Hz, 1H, 9-Flu—C*H*), 3.32 (m, 4H, 1-Ind—C*H*, OCH_3), 2.28–2.16 (m, 2H, IndCH_2CH_2Flu, $CH_2CH_2CH_3$), 2.05–1.98 (m, 2H, IndCH_2CH_2Flu, $CH_2CH_2CH_3$), 1.80–1.69 (m, 1H, IndCH_2CH_2Flu), 1.64 (s, 3H, CCH_3), 1.43–1.32 (m, 1H, IndCH_2CH_2Flu), 1.15–1.02 (m, 2H, $CH_2CH_2CH_3$), 0.85 (t, J = 7.3 Hz, 3H, $CH_2CH_2CH_3$). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ 158.6 (2-Ph—*C*), 150.9 (7a-Ind—*C*), 148.6 (3a-Ind—*C*), 147.1 (8a,9a-Flu—*C*), 144.3 (3-Ind—*C*), 141.23 and 141.20 (4a,4b-Flu—*C*), 135.0 (1-Ph—*C*), 130.8 (2-Ind—*C*), 128.1 (6-Ph—*C*), 127.4 (4-Ph—*C*), 126.9 (3,6-Flu—*C*), 126.84 and 126.82 (2,7-Flu—*C*), 125.5 (5-Ind—*C*), 124.34 and 124.30 (4,5-Flu—*C*), 123.6 (6-Ind—*C*), 122.4 (4-Ind—*C*), 121.4 (7-Ind—*C*), 120.3 (5-Ph—*C*), 119.81 and 119.78 (1,8-Flu—*C*), 112.1 (3-Ph—*C*), 55.0 (OCH_3), 47.9 (1-Ind—CH_2), 47.5 (9-Flu—*C*H), 42.6 (CH_2CCH_3), 41.1 ($CH_2CH_2CH_3$), 29.7 ($PhCH_2CH_2$), 27.1 ($PhCH_2CH_2$), 25.5 (CCH_3), 17.9 ($CH_2CH_2CH_3$), 14.8 ($CH_2CH_2CH_3$).

*1-(9-Fluorenyl)-2-{1-[3-(3-(3-(2-methoxyphenyl)pentyl))indenyl]} ethane (**L^{9}H$_2$**)*

Following the procedure described above, *n*-BuLi (11.5 ml, 2.39 mol l^{-1}, 27.5 mmol), 2-bromoanisole (5.09 g, 27.2 mmol) and 6,6-diethylbenzofulvene (3.99 g, 21.7 mmol) were used. The product of 3-{3-[3-(2-methoxyphenyl)pentyl]}indene (**Ind 9**) was recrystallized with diethyl ether to give an off-white powder (3.23 g, 51.0%). This compound was analyzed by ^{1}H NMR spectroscopy and was used without further purification.

A yellow solid was produced analogously to **L^{1}H$_2$** in 41.3% yield (1.23 g) from **Ind 9** (1.92 g, 6.57 mmol), *n*-BuLi (2.75 ml, 2.39 mol l^{-1}, 6.57 mmol) and 9-(2-bromoethyl)- fluorene (1.55 g, 5.67 mmol) were reacted to afford the product as a yellow solid (1.27 g, 48.6%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 7.76 (dd, J = 7.2, 2.9 Hz, 2H, 4,5-Flu—*H*), 7.53 (d, J = 7.4 Hz, 1H, 1-Flu—*H*), 7.48–7.44 (m, 2H, 7-Ind—*H*, 8-Flu—*H*), 7.39–7.28 (m, 4H, 2,3,6,7-Flu—*H*), 7.21–7.16 (m, 2H, 6-Ind—*H*, 6-Ph—*H*), 6.99–6.95 (m, 2H, 4,5-Ph—*H*), 6.84 (t, J = 7.5 Hz, 1H, 5-Ind—*H*), 6.69 (d, J = 7.5 Hz, 1H, 3-Ph—*H*), 6.45 (d, J = 7.6 Hz, 1H, 4-Ind—*H*), 6.26 (d, J = 1.9 Hz, 1H, 2-Ind—C*H*), 4.03 (t, J = 5.4 Hz, 1H, 9-Flu—C*H*), 3.35–3.33 (m, 1H, 1-Ind—CH_2), 3.21 (s, 3H, OCH_3), 2.34–2.20 (m, 3H, CH_2CH_3, CH_2CH_2), 2.12–1.98 (m, 3H, CH_2CH_3, CH_2CH_2), 1.77–1.68 (m, 1H, CH_2CH_2), 1.33–1.24 (m, 1H, CH_2CH_2), 0.66–0.61 (m, 6H, $C(CH_2CH_3)_2$). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ 158.6 (2-Ph—*C*), 148.56 (7a-Ind—*C*), 148.55 (3a-Ind—*C*), 147.06 and 147.05 (8a,9a-Flu—*C*), 144.3 (3-Ind—*C*), 141.23 and 141.21 (4a,4b-Flu—*C*), 133.9 (1-Ph—*C*), 132.3 (2-Ind—*C*), 128.8 (6-Ph—*C*), 127.3 (4-Ph—*C*), 126.9 (3,6-Flu—*C*), 126.83 and 126.81 (2,7-Flu—*C*), 125.4 (5-Ind—*C*), 124.3 and 124.2 (4,5-Flu—*C*), 123.5 (6-Ind—*C*), 122.3 (4-Ind—*C*), 121.2 (7-Ind—*C*), 120.1 (5-Ph—*C*), 119.80 and 119.76 (1,8-Flu—*C*), 112.2 (3-Ph—*C*), 55.0 (OCH_3), 48.0 (1-Ind—CH_2), 47.5 (9-Flu—*C*H), 45.8 ($C(C_2H_5)$), 30.0 (CH_2CH_2), 27.3 (CH_2CH_2), 25.4 (CH_2CH_3), 25.2 (CH_2CH_3), 8.54 (CH_2CH_3), 8.46 (CH_2CH_3).

Synthesis of Complexes

*Ethylene-1-(9-fluorenyl)-2-{1-[3-(2-(2-phenylpropyl))indenyl]} zirconium dichloride (**1**)*

To a solution of **L^{1}H$_2$** (1.16 g, 2.72 mmol) in 25 ml dry Et_2O at 0°C was added dropwise a solution of *n*-BuLi in *n*-hexane (2.53 ml, 2.15 mol l^{-1}, 5.44 mmol). The resulting suspension was stirred for 6 h at r.t. The solvent was removed under vacuum, and the residue was washed with 2 × 10 ml portions of dry petroleum ether and dried under vacuum. The obtained yellow solid was suspended in 20 ml dry Et_2O and cooled to 0°C. $ZrCl_4$ (0.67 g, 2.88 mmol) was added as solid. The orange suspension was stirred overnight at r.t. and the solvent was removed by filtration. The residue was extracted with dry CH_2Cl_2 and filtrated. The filtrate was concentrated and stored at −20°C to give the product as a red crystalline solid (0.245 g, 15.4%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 8.07 (d, J = 8.6 Hz, 1H, 7-Ind—*H*), 7.92 (d, J = 8.4 Hz, 1H, 4-Flu—*H*), 7.88 (d, J = 8.6 Hz, 1H, 1-Flu—*H*), 7.78 (d, J = 8.4 Hz, 1H, 5-Flu—*H*), 7.68–7.65 (m, 1H, 3-Flu—*H*), 7.51 (d, J = 8.6 Hz, 1H, 8-Flu—*H*), 7.46–7.42 (m, 1H, 2-Flu—*H*), 7.30–7.27 (m, 1H, 6-Flu—*H*), 7.10–7.04 (m, 4H, 7-Flu—*H*, 6-Ind—*H*, 3,5-Ph—*H*), 7.01–6.96 (m, 2H, 4-Ind—*H*, 4-Ph—*H*), 6.92–6.86 (m, 3H, 5-Ind—*H*, 2,6-Ph—*H*), 6.23 (s, 1H, 2-Ind—C*H*), 4.74–4.66 (m, 1H, CH_2CH_2), 4.27–4.181 (m, 1H, CH_2CH_2), 4.04–3.96 (m, 2H, CH_2CH_2), 1.96 (s, 3H, CH_3), 1.56 (s, 3H, CH_3). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ 151.0 (1-Ph—*C*), 128.9 (7-Ind—*C*), 128.6 (4b-Flu—*C*), 127.8 (3,5-Ph—*C*), 127.7 (4a-Flu—*C*), 127.6 (4-Flu—*C*), 127.1 (8a,9a-Flu—*C*), 126.7 (1-Flu—*C*), 126.1 (7a-Ind—*C*), 125.92 (5-Flu—*C*), 125.86 (3a-Ind—*C*), 125.7 (3-Flu—*C*), 125.6 (2,6-Ph—*C*), 125.4 (8-Flu—*C*), 125.1 (4-Ph—*C*), 124.9 (2-Flu—*C*), 124.8 (6-Flu—*C*), 124.2 (6-Ind—*C*), 124.1 (5-Ind—*C*), 123.9 (9-Flu—*C*), 123.2 (1-Ind—*C*), 123.1 (7-Flu—*C*), 121.6 (4-Ind—*C*), 121.3 (3-Ind—*C*), 117.5 (2-Ind—*C*), 41.0 ($C(CH_3)_2$), 32.2 (CH_2CH_2), 31.2 (CH_2CH_2), 30.0 ($C(CH_3)_2$), 25.6 ($C(CH_3)_2$). Anal. Calcd for $C_{33}H_{28}Cl_2Zr{\cdot}0.9CH_2Cl_2$: C, 61.40; H, 4.53; found: C, 61.58; H, 4.45%.

*Ethylene-1-(9-fluorenyl)-2-{1-[3-(2-(2-phenylpentyl))indenyl]} zirconium dichloride (**2**)*

Following the procedure described above, **L^{2}H$_2$** (1.13 g, 2.49 mmol), *n*-BuLi (2.80 ml, 1.79 mol l^{-1}, 4.97 mmol)) and $ZrCl_4$ (0.65 g, 2.78 mmol) were reacted to afford the product as red crystals (0.858 g, 56.3%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 8.07 (d, J = 8.4 Hz, 1H, 7-Ind—*H*), 7.91 (dd, J = 8.4, 2.8 Hz, 2H, 1,4-Flu—*H*), 7.77 (d, J = 8.4 Hz, 1H, 5-Flu—*H*), 7.67 (t, J = 7.2 Hz, 1H, 3-Flu—*H*), 7.49 (d, J = 8.6 Hz, 1H, 8-Flu—*H*), 7.46 (t, J = 7.8 Hz, 1H, 2-Flu—*H*), 7.28 (t, J = 7.2 Hz, 1H, 6-Flu—*H*), 7.07–7.02 (m, 3H, 7-Flu—*H*, 3,5-Ph—*H*), 6.98-6.93 (m, 3H, 4,6-Ind—*H*, 4-Ph—*H*), 6.88 (d, J = 7.2 Hz, 2H, 2,6-Ph—*H*), 6.84 (t, J = 8.0 Hz, 1H, 5-Ind—*H*), 6.29 (s, 1H, 2-Ind—*H*), 4.76–4.67 (m, 1H, CH_2Flu), 4.29-4.20 (m, 1H, CH_2Ind), 3.95 (dd, J = 14.7, 7.7 Hz, 2H, IndCH_2CH_2Flu), 2.34 (dt, J = 12.4, 4.9 Hz, 1H, $CH_2CH_2CH_3$), 1.88 (s, 3H, CCH_3), 1.71 (dt, J = 12.4, 3.4 Hz, 1H, $CH_2CH_2CH_3$), 1.24–1.14 (m, 1H, $CH_2CH_2CH_3$), 0.72 (t, J = 7.2 Hz, 3H, $CH_2CH_2CH_3$), 0.66-0.55 (m, 1H, $CH_2CH_2CH_3$). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ 148.4 (1-Ph—*C*), 131.5 (7a-Ind—*C*), 128.9 (7-Ind—*C*), 128.3 and 127.6 (4a,4b-Flu—*C*), 127.5 (3,5-Ph—*C*), 127.4 (4-Flu—*C*), 126.7 (1-Flu—*C*), 126.5 (2,6-Ph—*C*), 126.09 and 126.05 (8a,9a-Flu—*C*), 125.8 (3a-Ind—*C*), 125.5 (4-Ph—*C*), 125.2 (5-Flu—*C*), 125.1 (3-Flu—*C*), 124.9 (8-Flu—*C*), 124.6 (2-Flu—*C*), 124.04 (6-Ind—*C*), 124.02 (5-Ind—*C*), 123.96 (4-Ind—*C*), 123.3 (9-Flu—*C*), 123.2 (6-Flu—*C*), 121.8 (7-Flu—*C*), 121.2 (1-Ind—*C*), 117.4 (3-Ind—*C*), 103.7 (2-Ind—*C*), 43.9 ($CH_3CCH_2CH_2CH_3$), 43.4 ($CH_3CCH_2CH_2CH_3$), 32.5 (CH_2CH_2), 30.1 (CH_2CH_2), 21.5 (CCH_3), 16.6 ($CH_2CH_2CH_3$), 14.6 ($CH_2CH_2CH_3$). Anal. Calcd for $C_{35}H_{32}Cl_2Zr$: C, 68.38; H, 5.25; found: C, 68.18; H, 5.09%.

*Ethylene-1-(9-fluorenyl)-2-{1-[3-(3-(3-phenylpentyl))indenyl]} zirconium dichloride (**3**)*

Following the procedure described above, **L^{3}H$_2$** (0.98 g, 2.16 mmol), *n*-BuLi (1.80 ml, 2.39 mol l^{-1}, 4.30 mmol) and $ZrCl_4$ (0.54 g,

2.32 mmol) were reacted to afford the product as red crystals (0.406 g, 30.6%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 8.02 (d, J = 8.6 Hz, 1H, 7-Ind—*H*), 7.93 (d, J = 8.4 Hz, 1H, 4-Flu—*H*), 7.86 (d, J = 8.4 Hz, 1H, 1-Flu—*H*), 7.79 (d, J = 8.4 Hz, 1H, 5-Flu—*H*), 7.68 (t, J = 7.6 Hz, 1H, 3-Flu—*H*), 7.58 (d, J = 7.2 Hz, 2H, 3,5-Ph—*H*), 7.53 (d, J = 8.6 Hz, 1H, 8-Flu—*H*), 7.45 (t, J = 7.6 Hz, 1H, 2-Flu—*H*), 7.28(t, J = 7.5 Hz, 1H, 6-Flu—*H*), 7.21–7.14 (m, 3H, 2,4,6-Ph—*H*), 7.07 (t, J = 7.6 Hz, 1H, 7-Flu—*H*), 6.94 (t, J = 7.5 Hz, 1H, 6-Ind—*H*), 6.81 (t, J = 7.5 Hz, 1H, 5-Ind—*H*), 6.40 (d, J = 8.6 Hz, 1H, 4-Ind—*H*), 6.13 (s, 1H, 2-Ind—*H*), 4.69-4.60 (m, 1H, CH_2Flu), 4.22–4.13 (m, 1H, CH_2Ind), 4.00–3.93 (m, 2H, IndCH_2CH_2Flu), 2.64–2.54 (m, 1H, CH_2CH_3), 2.10–1.99 (m, 2H, CH_2CH_3), 1.83–1.74 (m, 1H, CH_2CH_3), 0.48 (t, J = 7.4 Hz, 3H, CH_2CH_3), 0.32 (t, J = 7.4 Hz, 3H, CH_2CH_3). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ 144.7 (1-Ph—*C*), 131.4 (7a-Ind—*C*), 129.0 (1,4-Flu—*C*), 128.8 (4b-Flu—*C*), 128.7 (7-Ind—*C*), 127.8 (3,5-Ph—*C*), 127.71 (4a-Flu—*C*), 127.66 (5-Flu—*C*), 126.7 (3-Flu—*C*), 126.4 (9a-Flu—*C*), 126.0 (2,6-Ph—*C*), 125.7 (8-Flu—*C*), 125.5 (8a-Flu—*C*), 125.13 (6-Ind—*C*), 125.09 (2-Flu—*C*), 124.72 (4-Ph—*C*), 124.69 (3a-Ind—*C*), 123.97 (5-Ind—*C*), 123.95 (6-Flu—*C*), 123.3 (4-Ind—*C*), 123.1 (9-Flu—*C*), 121.6 (7-Flu—*C*), 121.1 (1-Ind—*C*), 117.2 (3-Ind—*C*), 103.9 (2-Ind—*C*), 49.8 ($C(C_2H_5)$), 32.3 (CH_2CH_2), 30.8 (CH_2CH_3), 30.0 (CH_2CH_2), 27.7 (CH_2CH_3), 9.3 (CH_2CH_3), 8.1 (CH_2CH_3). Anal. Calcd for $C_{35}H_{32}Cl_2Zr$: C, 68.38; H, 5.25; found: C, 68.29; H, 5.23%.

*Ethylene-1-(9-fluorenyl)-2-{1-[3-(2-(2-(2-methylphenyl)propyl))indenyl]}zirconium dichloride (**4**)*

Following the procedure described above, **L^4H_2** (1.89 g, 4.29 mmol), *n*-BuLi (3.60 ml, 2.39 mol l^{-1}, 8.60 mmol) and $ZrCl_4$ (1.03 g, 4.42 mmol) were reacted to afford the product as red crystals (0.97 g, 34.4%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 8.13 (d, J = 8.6 Hz, 1H, 7-Ind—*H*), 7.89 (d, J = 7.4 Hz, 2H, 1,4-Flu—*H*), 7.76 (d, J = 8.4 Hz, 1H, 5-Flu—*H*), 7.68–7.64 (m, 1H, 3-Flu—*H*), 7.50 (d, J = 8.6 Hz, 1H, 8-Flu—*H*), 7.46–7.42 (m, 2H, 2-Flu—*H*, 6-Ph—*H*), 7.30–7.26 (m, 1H, 6-Flu—*H*), 7.10–7.02 (m, 2H, 7-Flu—*H*, 5-Ph—*H*), 7.00–6.94 (m, 2H, 6-Ind—*H*, 4-Ph—*H*), 6.90–6.82 (m, 2H, 4,5-Ind—*H*), 6.75 (dd, J = 7.4, 0.6 Hz, 1H, 3-Ph—*H*), 6.28 (s, 1H, 2-Ind—*H*), 4.75–4.66 (m, 1H, CH_2Flu), 4.28–4.19 (m, 1H, CH_2Ind), 4.00–3.94 (m, 2H, IndCH_2CH_2Flu), 2.03 (s, 3H, $C(CH_3)_2$), 1.65 (s, 3H, $C(CH_3)_2$), 1.51 (s, 3H, Ph—CH_3). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ 147.5 (1-Ph—*C*), 136.2 (2-Ph—*C*), 132.6 (6-Ph—*C*), 131.8 (7a-Ind—*C*), 129.0 (7-Ind—*C*), 127.5 and 127.4 (4a,4b-Flu—*C*), 127.2 (1-Flu—*C*), 127.0 (4-Flu—*C*), 126.5 (9a-Flu—*C*), 126.1 (5-Flu—*C*), 126.0 (3-Flu—*C*), 125.8 (8a-Flu—*C*), 125.7 (6-Ind—*C*), 125.6 (8-Flu—*C*), 125.3 (5-Ph—*C*), 125.0 (4-Ph—*C*), 124.9 (2-Flu—*C*), 124.5 (3-Ph—*C*), 124.2 (6-Flu—*C*), 124.0 (5-Ind—*C*), 123.42 (9-Flu—*C*), 123.40 (4-Ind—*C*), 123.38 (1-Ind—*C*), 122.0 (3a-Ind—*C*), 120.1 (3-Ind—*C*), 119.4 (7-Flu—*C*), 104.1 (2-Ind—*C*), 41.0 ($C(CH_3)_2$), 32.8 (CH_2CH_2), 29.9 (CH_2CH_2), 29.1 ($C(CH_3)_2$), 27.1 ($C(CH_3)_2$), 22.2 ($PhCH_3$). Anal. Calcd for $C_{34}H_{30}Cl_2Zr{\cdot}0.25CH_2Cl_2$: C, 66.14; H, 4.94; found: C, 66.35; H, 4.83%.

*Ethylene-1-(9-fluorenyl)-2-{1-[3-(2-(2-(2-methylphenyl)pentyl))indenyl]}zirconium dichloride (**5**)*

Following the procedure described above, **L^5H_2** (1.10 g, 2.35 mmol), *n*-BuLi (2.65 ml, 1.79 mol l^{-1}, 4.74 mmol) and $ZrCl_4$ (0.57 g, 2.45 mmol) were reacted to afford the product as red crystals (0.372 g, 25.2%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 8.13 (d, J = 8.7 Hz, 1H, 7-Ind—*H*), 7.89 (d, J = 8.6 Hz, 2H, 1,4-Flu—*H*), 7.76(d, J = 8.4 Hz, 1H, 5-Flu—*H*), 7.66 (dt, J = 8.2, 1.0 Hz, 1H, 3-Flu—*H*), 7.51–7.44 (m, 3H, 2,8-Flu—*H*, 6-Ph—*H*), 7.28 (dt, J = 6.9, 0.8 Hz, 1H, 6-Flu—*H*), 7.08 (dt, J = 8.0, 1.0 Hz, 1H, 7-Flu—*H*), 7.05–7.02 (m, 1H, 5-Ph—*H*), 6.98–6.93 (m, 2H, 6-Ind—*H*, 4-Ph—*H*), 6.85–6.78 (m, 2H, 4,5-Ind—*H*), 6.69 (dd, J = 7.4, 0.6 Hz, 1H, 3-Ph—*H*), 6.35 (s, 1H, 2-Ind—*H*), 4.75–4.66 (m, 1H, CH_2Flu), 4.28–4.19 (m, 1H, CH_2Ind), 4.00–3.93 (m, 2H, IndCH_2CH_2Flu), 2.20–2.15 (m, 2H, $CH_2CH_2CH_3$), 1.97 (s, 3H, CCH_3), 1.41 (s, 3H, Ph—CH_3), 1.25–1.16 (m, 1H, $CH_2CH_2CH_3$), 0.75 (t, J = 7.2 Hz, 3H, $CH_2CH_2CH_3$), 0.60–0.49 (m, 1H, $CH_2CH_2CH_3$). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ 144.7 (1-Ph—*C*), 136.5 (2-Ph—*C*), 132.5 (6-Ph—*C*), 131.8 (7a-Ind—*C*), 128.9 (7-Ind—*C*), 128.6 (1-Flu—*C*), 127.8 (4-Flu—*C*), 127.3 (4a,4b-Flu—*C*), 127.1 (5-Ph—*C*), 126.9 (5-Flu—*C*), 126.6 (9a-Flu—*C*), 126.0 (3-Flu—*C*), 125.8 (8a-Flu—*C*), 125.41 (8-Flu—*C*), 125.37 (6-Ind—*C*), 125.1 (2-Flu—*C*), 125.0 (6-Flu—*C*), 124.8 (4-Ph—*C*), 124.5 (5-Ind—*C*), 124.3 (3-Ph—*C*), 124.0 (4-Ind—*C*), 123.5 and 123.4 (9-Flu—*C*, 1-Ind—*C*), 122.0 (3a-Ind—*C*), 120.0 (3-Ind—*C*), 119.1 (7-Flu—*C*), 104.2 (2-Ind—*C*), 44.3 ($CH_3CCH_2CH_2CH_3$), 39.1 ($CH_3CCH_2CH_2CH_3$), 33.0 (CH_2CH_2), 29.9 (CH_2CH_2), 25.5 (CCH_3), 22.1 (Ph—CH_3), 17.3 ($CH_2CH_2CH_3$), 14.7 ($CH_2CH_2CH_3$). EI/HRMS: $[M]^+$ calcd for $C_{36}H_{34}Cl_2Zr$, 626.1085; found, 626.1088.

*Ethylene-1-(9-fluorenyl)-2-{1-[3-(3-(3-(2-methylphenyl)pentyl))indenyl]} zirconium dichloride (**6**)*

Following the procedure described above, **L^6H_2** (0.99 g, 2.11 mmol), *n*-BuLi (1.77 ml, 2.39 mol l^{-1}, 4.23 mmol) and $ZrCl_4$ (0.50 g, 2.15 mmol) were reacted to afford the product as red crystals (0.71 g, 53.1%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 8.06 (d, J = 8.6 Hz, 1H, 7-Ind—*H*), 7.89 (d, J = 8.4 Hz, 1H, 4-Flu—*H*), 7.87 (d, J = 8.6 Hz, 1H, 1-Flu—*H*), 7.76 (d, J = 8.4 Hz, 1H, 5-Flu—*H*), 7.66 (t, J = 7.6 Hz, 1H, 3-Flu—*H*), 7.54 (d, J = 8.6 Hz, 1H, 8-Flu—*H*), 7.47 (d, J = 8.6 Hz, 1H, 6-Ph—*H*), 7.42 (t, J = 7.6 Hz, 1H, 2-Flu—*H*), 7.29 (t, J = 7.7 Hz, 1H, 6-Flu—*H*), 7.10 (t, J = 5.6 Hz, 1H, 7-Flu—*H*), 7.08 (t, J = 5.6 Hz, 1H, 5-Ph—*H*), 6.98 (t, J = 7.2 Hz, 1H, 4-Ph—*H*), 6.93 (dd, J = 8.4, 4.0 Hz, 1H, 4-Ph—*H*), 6.84 (d, J = 3.6 Hz, 2H, 4,5-Ind—*H*), 6.75 (d, J = 7.4 Hz, 1H, 3-Ph—*H*), 6.18 (s, 1H, 2-Ind—*H*), 4.74–4.65 (m, 1H, CH_2Flu), 4.26–4.17 (m, 1H, CH_2Ind), 3.95 (dd, J = 14.6, 7.8 Hz, 2H, IndCH_2CH_2Flu), 2.69–2.60 (m, 1H, CH_2CH_3), 2.58–2.48 (m, 1H, CH_2CH_3), 2.39–2.30 (m, 1H, CH_2CH_3), 2.21–2.12 (m, 1H, CH_2CH_3), 1.30 (s, 3H, Ph—CH_3), 1.06 (t, J = 7.3 Hz, 3H, CH_2CH_3), 0.60 (t, J = 7.4 Hz, 3H, CH_2CH_3). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ 142.2 (1-Ph—*C*), 137.1 (2-Ph—*C*), 132.6 (6-Ph—*C*), 131.1 (7a-Ind—*C*), 129.1 (7-Ind—*C*), 128.8 (1-Flu—*C*), 127.9 (4a,4b-Flu—*C*), 127.6 (4-Flu—*C*), 126.8 (5-Flu—*C*), 126.3 (9a-Flu—*C*), 126.2 (3-Flu—*C*), 125.9 (5-Ph—*C*), 125.60 (8-Flu—*C*), 125.57 (8a-Flu—*C*), 125.2 (6-Ind—*C*), 125.04 (2-Flu—*C*), 124.98 (6-Flu—*C*), 124.5 (4-Ph—*C*), 124.0 (5-Ind—*C*), 123.9 (3-Ph—*C*), 123.6 (9-Flu—*C*), 123.2 (1-Ind—*C*), 123.0 (4-Ind—*C*), 121.7 (3a-Ind—*C*), 120.8 (3-Ind—*C*), 118.5 (7-Flu—*C*), 104.3 (2-Ind—*C*), 49.0 ($C(C_2H_5)$), 32.8 (CH_2CH_2), 31.4 (CH_2CH_3), 30.5 (CH_2CH_3), 30.0 (CH_2CH_2), 21.8 (Ph—CH_3), 11.7 (CH_2CH_3), 10.2 (CH_2CH_3). Anal. Calcd for $C_{36}H_{34}Cl_2Zr{\cdot}0.5CH_2Cl_2$: C, 65.31; H, 5.26; found: C, 65.40; H, 5.32%.

*Ethylene-1-(9-fluorenyl)-2-{1-[3-(2-(2-(2-methoxylphenyl)propyl))indenyl]} zirconium dichloride (**7**)*

Following the procedure described above, **L^7H_2** (0.84 g, 1.84 mmol), *n*-BuLi (2.33 ml, 1.59 mol l^{-1}, 3.68 mmol), and $ZrCl_4$ (0.44 g, 1.89 mmol) were reacted to afford the product as red crystals (0.234 g, 20.6%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 8. 07 (d, J = 8.6 Hz, 1H, 7-Ind—*H*), 7.89 (t, J = 8.4 Hz, 2H, 1,4-Flu—*H*), 7.76 (d, J = 8.4 Hz, 1H, 5-Flu—*H*), 7.66 (t, J = 7.6 Hz, 1H, 3-Flu—*H*), 7.50 (d, J = 8.4 Hz, 1H, 8-Flu—*H*), 7.45 (t, J = 7.6 Hz, 1H, 2-Flu—*H*),

7.28 (t, J = 7.4 Hz, 1H, 6-Flu—*H*), 7.22 (d, J = 8.0 Hz, 1H, 6-Ph—*H*), 7.08-7.01 (m, 3H, 7-Flu—*H*, 3,5-Ph—*H*), 6.94 (t, J = 7.6 Hz, 1H, 6-Ind—*H*), 6.86 (t, J = 7.6 Hz, 1H, 5-Ind—*H*), 6.82 (t, J = 8.0 Hz, 1H, 4-Ph—*H*), 6.55 (d, J = 8.0 Hz, 1H, 4-Ind—*H*), 6.26 (s, 1H, 2-Ind—*H*), 4.73–4.65 (m, 1H, CH_2Flu), 4.27–4.19 (m, 1H, CH_2Ind), 4.01–3.93 (m, 2H, IndCH_2CH_2Flu), 3.21 (s, 3H, OCH_3), 1.97 (s, 3H, $C(CH_3)_2$), 1.68 (s, 3H, $C(CH_3)_2$). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ 157.8 (2-Ph—*C*), 138.0 (7a-Ind—*C*), 131.3 (1-Ph—*C*), 128.8 (1-Flu—*C*), 127.5 and 127.4 (4a,4b-Flu—*C*), 127.3 (4-Flu—*C*), 127.2 (7-Ind—*C*), 126.6 (5-Flu—*C*), 126.5 (3-Flu—*C*), 126.1 and 125.9 (8a,9a-Flu—*C*), 125.5 (8-Flu—*C*), 125.3 (6-Ph—*C*), 125.0 (2-Flu—*C*), 124.7 (6-Flu—*C*), 124.2 (4-Ph—*C*), 124.1 (6-Ind—*C*), 124.0 (5-Ind—*C*), 123.5 (3a-Ind—*C*), 123.20 and 123.19 (9-Flu—*C*,1-Ind—*C*), 121.7 (4-Ind—*C*), 120.5 (5-Ph—*C*), 120.2 (3-Ind—*C*), 119.6 (7-Flu—*C*), 112.4 (3-Ph—*C*), 103.6 (2-Ind—*C*), 54.8 (OCH_3), 39.9 ($C(CH_3)_2$), 32.3 (CH_2CH_2), 30.0 ($C(CH_3)_2$), 27.1 ($C(CH_3)_2$), 26.3 (CH_2CH_2). Anal. Calcd for $C_{34}H_{30}OCl_2Zr$: C, 66.21; H, 4.90; found: C, 66.02; H, 4.95%.

*Ethylene-1-(9-fluorenyl)-2-{1-[3-(2-(2-methoxylphenyl)pentyl))indenyl]} zirconium dichloride (**8**)*

Following the procedure described above, $\mathbf{L^8H_2}$ (0.84 g, 1.84 mmol), *n*-BuLi (2.33 ml, 1.59 mol l^{-1}, 3.68 mmol), and $ZrCl_4$ (0.44 g, 1.89 mmol) were reacted to afford the product as red crystals (0.234 g, 20.6%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 8. 08 (d, J = 8.6 Hz, 1H, 7-Ind—*H*), 7.89 (t, J = 8.8 Hz, 2H, 1,4-Flu—*H*), 7.75 (d, J = 8.4 Hz, 1H, 5-Flu—*H*), 7.66 (t, J = 7.5 Hz, 1H, 3-Flu—*H*), 7.48 (d, J = 8.6 Hz, 1H, 8-Flu—*H*), 7.45 (t, J = 7.8 Hz, 1H, 2-Flu—*H*), 7.38 (d, J = 7.8 Hz, 1H, 6-Ph—*H*), 7.29–7.25 (m, 1H, 6-Flu—*H*), 7.04 (t, J = 7.2 Hz, 1H, 7-Flu—*H*), 7.02 (t, J = 7.2 Hz, 1H, 5-Ph—*H*), 6.94 (d, J = 8.6 Hz, 1H, 4-Ind—*H*), 6.91 (t, J = 8.4 Hz, 1H, 4-Ph—*H*), 6.86 (t, J = 7.6 Hz, 1H, 6-Ind—*H*), 6.80 (t, J = 7.8 Hz, 1H, 5-Ind—*H*), 6.48 (d, J = 8.1 Hz, 1H, 3-Ph—*H*), 6.33 (s, 1H, 2-Ind—*H*), 4.75–4.66 (m, 1H, CH_2Flu), 4.30–4.21 (m, 1H, CH_2Ind), 4.00–3.90 (m, 2H, IndCH_2CH_2Flu), 3.04 (s, 3H, OCH_3), 2.36 (dt, J = 12.5, 4.0 Hz, 1H, $CH_2CH_2CH_3$), 2.14 (dt, J = 12.5, 4.0 Hz, 1H, $CH_2CH_2CH_3$), 1.90 (s, 3H, CCH_3), 1.23–1.13 (m, 1H, $CH_2CH_2CH_3$), 0.74 (t, J = 7.2 Hz, 3H, $CH_2CH_2CH_3$), 0.62–0.50 (m, 1H, $CH_2CH_2CH_3$). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ 158.0 (2-Ph—*C*), 135.7 (7a-Ind—*C*), 131.3 (1-Ph—*C*), 128.8 (6-Ph—*C*), 128.1 (1-Flu—*C*), 127.4 (4a-Flu—*C*), 127.3 (7-Ind—*C*), 127.12 (4b-Flu—*C*), 127.08 (4,5-Flu—*C*), 127.0 (3-Flu—*C*), 126.9 and 126.8 (8a,9a-Flu—*C*), 126.7 (8-Flu—*C*), 125.4 (2-Flu—*C*), 125.1 (6-Flu—*C*), 125.0 (4-Ph—*C*), 124.7 (6-Ind—*C*), 124.2 (5-Ind—*C*), 124.1 (9-Flu—*C*), 123.9 (1-Ind—*C*), 123.2 (3a-Ind—*C*), 121.9 (4-Ind—*C*), 120.4 (5-Ph—*C*), 120.0 (3-Ind—*C*), 119.5 (7-Flu—*C*), 112.5 (3-Ph—*C*), 103.6 (2-Ind—*C*), 54.9 (OCH_3), 43.1 (CCH_3), 38.5 ($CH_2CH_2CH_3$), 32.5 ($PhCH_2CH_2$), 30.0 ($PhCH_2CH_2$), 23.6 (CCH_3), 17.4 ($CH_2CH_2CH_3$), 14.7 ($CH_2CH_2CH_3$). Anal. Calcd for $C_{36}H_{34}OCl_2Zr{\cdot}0.1CH_2Cl_2$: C, 66.37; H, 5.28; found: C, 66.05; H, 5.28%.

*Ethylene-1-(9-fluorenyl)-2-{1-[3-(3-(3-(2-oxy-phenyl)pentyl))indenyl]}zirconium chloride (**9**)*

Following the procedure described above, $\mathbf{L^9H_2}$ (1.10 g, 2.27 mmol), *n*-BuLi (1.90 ml, 2.39 mol l^{-1}, 4.54 mmol), and $ZrCl_4$ (0.53 g, 2.27 mmol) were reacted to afford the product as yellow crystals (0.214 g, 15.9%). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 8.04 (d, J = 8.4 Hz, 1H, 7-Ind—*H*), 7.98 (d, J = 8.2 Hz, 1H, 4-Flu—*H*), 7.83 (d, J = 8.2 Hz, 1H, 1-Flu—*H*), 7.70 (d, J = 8.4 Hz, 1H, 5-Flu—*H*), 7.40 (d, J = 6.8 Hz, 1H, 6-Ph—*H*), 7.38–7.28 (m, 4H, 2,3,6,7-Flu—*H*), 7.22 (d, J = 7.7 Hz, 1H, 8-Flu—*H*), 6.96 (t, J = 7.7 Hz, 1H, 6-Ind—*H*), 6.93–6.89 (m, 1H, 5-Ind—*H*), 6.77–6.70 (m, 3H, 4-Ind—*H*, 4,5-Ph—*H*), 6.62 (br s, 1H, 2-Ind—*H*), 6.12 (d, J = 8.0 Hz, 1H, 3-Ph—*H*), 4.20–4.07 (m, 2H, IndCH_2CH_2Flu), 4.03–3.95 (m, 1H, CH_2CH_2), 3.66–3.57 (m, 1H, CH_2CH_2), 2.20–2.11 (m, 1H, CH_2CH_3), 2.06–1.97 (m, 1H, CH_2CH_3), 1.91–1.82 (m, 1H, CH_2CH_3), 1.51–1.40 (m, 1H, CH_2CH_3), 0.53 (t, J = 7.3 Hz, 3H, CH_2CH_3), 0.43 (t, J = 7.3 Hz, 3H, CH_2CH_3). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ 160.7 (2-Ph—*C*), 131.7 (7a-Ind—*C*), 128.4 (7-Ind—*C*), 127.6 (1,4-Flu—*C*), 127.4 (5-Flu—*C*), 126.8 (4a,4b-Flu—*C*), 126.7 (6-Ph—*C*), 126.5 (1-Ph—*C*), 125.8 (8a,9a-Flu—*C*), 124.9 (2,3-Flu—*C*), 124.8 (6,7-Flu—*C*), 124.4 (8-Flu—*C*), 124.1 (4-Ph—*C*), 123.7 (6-Ind—*C*), 123.5 (5-Ind—*C*), 122.8 (3a-Ind—*C*), 121.7 (4-Ind—*C*), 120.9 (9-Flu—*C*,1-Ind—*C*), 120.4 (3-Ind—*C*), 119.6 (5-Ph—*C*), 119.2 (2-Ind—*C*), 101.3 (3-Ph—*C*), 44.0 ($C(C_2H_5)$), 28.1 (CH_2CH_2), 27.6 (CH_2CH_2), 26.6 (CH_2CH_3), 25.6 (CH_2CH_3), 8.6 (CH_2CH_3), 8.1 (CH_2CH_3). Anal. Calcd for $C_{35}H_{31}OClZr{\cdot}1.2CH_2Cl_2$: C, 62.45; H, 4.84; found: C, 62.55; H, 4.97%.

General Oligomerization Procedures

A 100 ml stainless steel autoclave equipped with a magnetic stirrer was heated under vacuum for 1 h over 100°C, then allowed to cool to the required temperature under propylene atmosphere, and charged with 20 ml toluene. The reactor was sealed and pressurized to 6 bar of propylene pressure. Stirring for about 30 min ensured that the solution was equilibrated and the required reaction temperature was established. The propylene pressure was then released. An appropriate amount of MAO in toluene and the solution of zirconocene complex in 1 ml toluene were added sequentially. The reactor was sealed and pressurized to the required propylene pressure. After the reaction was carried out for 0.5 h, the reactor was cooled rapidly with an ice–salt bath to quench the further reaction and avoid any loss of possible low-boiling-point fraction. When the reactor was completely cooled down, the pressure was released and 1 ml of methanol was injected immediately. Heptane (0.2 ml) was added as internal standard. An aliquot of the reaction solution was withdrawn, filtered and then analyzed by GC. The residual bulk solution was quenched by the addition of 3% HCl–ethanol and washed three times with water. All the volatiles of the solution were evaporated to check the production of any higher-molecular-weight oligomers.

GC-MS Analysis

GC-MS analysis was performed on an Agilent 6890GC-5975MSD instrument (Agilent Technologies, USA). A fused silica capillary Agilent Technologies HP-5MS (5% phenyl methyl siloxane) column (30 m × 0.25 mm × 0.25 μm) was used for the separation.

The injection volume was 10 μl. The inlet temperature was maintained at 250°C. The column oven was held at 35°C for 2 min, and then increased to 50°C at a rate of 5.0°C min^{-1} and held for 3 min. The linear velocity of the helium carrier gas was 1.0 ml min^{-1} at a split ratio of 20:1. The mass spectrometer was used under the following conditions: ion source temperature, 230°C; scan range, *m/z* 10–550. The internal standard was heptane.

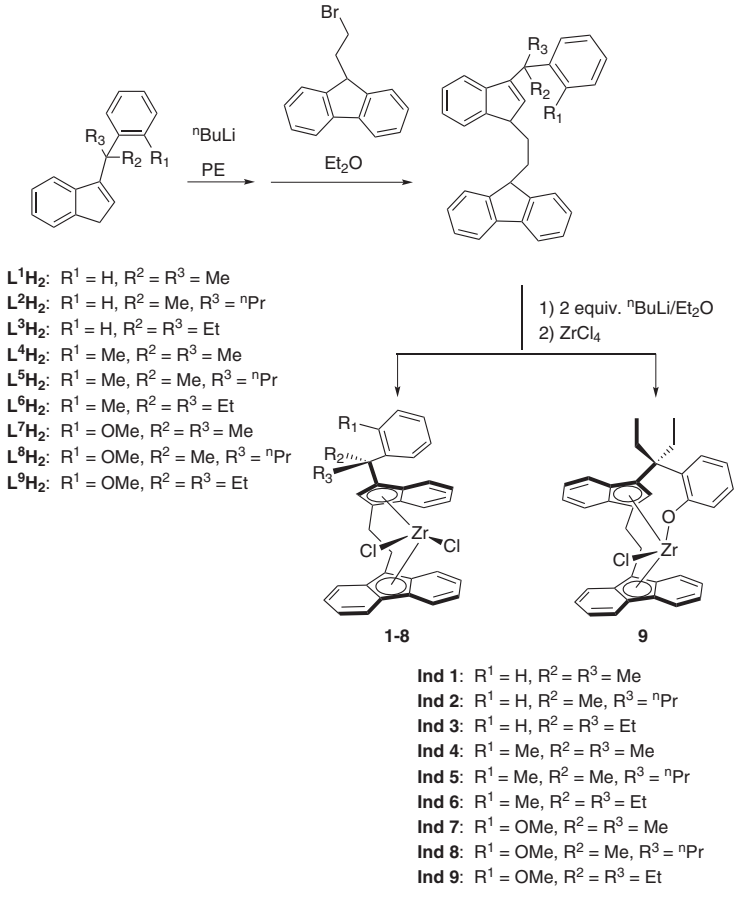
Components were identified by matching their recorded mass spectra with the standard mass spectra from the National Institute of Standards and Technology (NIST05.LIB) libraries data provided by the software of the GC-MS system, literature data and standards of the main components. The results were also confirmed based on their retention indices (determined with reference to a homologous series of normal alkanes) on HP-5MS capillary column. (Jayaprakasha *et al.*, 1997; Lazari *et al.*, 1999; Adams, 2001; Gallori *et al.*, 2001; Skaltsa *et al.*, 2003).[17]

Results and Discussion

Synthesis of Zirconium Complexes

The synthesis of substituted indene **Ind1–Ind9** and the relevant ethylene-bridged indenyl-fluorenyl proligands $\mathbf{L^1H_2}$–$\mathbf{L^9H_2}$ was accomplished via a procedure reported previously.[18] According to this method, the zirconocene complexes **1–8** were prepared via a straightforward reaction of $ZrCl_4$ with 1 equiv. of dilithium salt of the corresponding ligand in diethyl ether (Scheme 1), followed by an extraction and recrystallization in dichloromethane. In contrast to complexes **7** ($R^2 = R^3 = Me$) and **8** ($R^2 = Me$, $R^3 = {}^nPr$) bearing a pendant *o*-methoxyphenyl group on the indenyl ring, complex **9** ($R^2 = R^3 = Et$) with the same pentant group was obtained as a zircoxacyclic structure. A similar result was previously observed in the synthesis of titanocene complexes with analogous Cp ligands, where the presence of bigger ethyl groups on the quaternary carbon was suggested to promote an intramolecular elimination of a molecule of chloromethane to form a titanoxacyclic species.[19] All complexes **1–9** were characterized by ^1H,^{13}C NMR spectroscopy and elemental analysis or high-resolution mass spectroscopy.

Furthermore, the molecular structure of complex **4** was determined by X-ray diffraction study. As shown in Fig. 1, the bond lengths of Zr—C1, Zr—C2, Zr—C7, Zr—C8, Zr—C13 vary to a certain degree (2.427(2)–2.701(2) Å), which may evidence the coordination mode of the central five-membered ring of the fluorenyl slipping from η^5 towards η^3.



Scheme 1. Synthesis of complexes 1–9.

Propylene Dimerization

Propylene dimerization by zirconocene complexes **1–9** in the presence of MAO were explored. In general, C_1-symmetric *ansa*-(indenyl)(fluorenyl) zirconocene complexes (where indenyl, fluorenyl could also be substituted) are well known for their catalytic abilities of producing polypropylenes with various tacticities.[18] However, upon activation with MAO, these zirconocene complexes showed no activity for propylene polymerization or transformation in toluene at 30 and 60°C. Interestingly, when the polymerization temperature was increased to 100°C, the four sterically less encumbered C_1-symmetric zirconocene complexes **1**, **2**, **4** and **5** could catalyze the dimerization of propylene to produce 2-methyl-1-pentene with high selectivities ranging from 95.7% to 98.4% and moderate activities. There were no polymers or higher oligomers in the reaction end products, but with 4-methyl-2-pentene detected as the only byproduct. Among them, complex **4** displayed the highest dimerization activity of 7.89×10^4 g (mol-Zr·h)$^{-1}$ at an Al/Zr ratio of 8000 (Table 1, run 9), while complex **5** gave the highest selectivity for 2-methyl-1-pentene up to 98.4% (run 11). All results are listed in Table 1, and a typical GC trace of propylene dimer obtained by complex **4** is shown in Fig. 2.

It seems that the alkyl groups on the quaternary carbon bridge of the substituent have a significant influence on the catalytic performance of these zirconocene complexes. In comparison with complexes **1**, **2**, **4** and **5**, complexes **3** and **6** with two ethyl groups on the quaternary carbon bridge only afforded trace amount of propylene dimerization products under otherwise identical conditions (runs 5 and 12). The activities of complexes **1–3** decreased in the order **2** > **1** >> **3**, while for complexes **4–6** with a pendant *o*-methylphenyl group activity decreased with the increase of the steric bulkiness of the alkyl groups on the quaternary carbon.

Furthermore, neither complexes **7** and **8** bearing a pendant *o*-methoxyphenyl on the indenyl ring nor the zircoxacyclic complex **9** could show any catalytic activity for propylene transformation. According to our previous studies,[20] the introduction of the same type of substituent on a Cp or indenyl ring would easily lead to the formation of a metalloxacyclic complex via the elimination of a CH_3Cl molecule at higher reaction temperature; thus it is reasonable that in the cases of complexes **7** and **8** analogous zircoxacyclic structures might also be formed under the adopted polymerization conditions. Similar to complex **9**, the inert intramolecular Zr—O covalent bonding and the lack of two *cis*-located halogen ligands might prevent the formation of any catalytically active species. Moreover, some weak interactions between the methoxy group and MAO might also be the factor accounting for the deactivation of these zirconocene complexes.

In order to investigate the influence of reaction time on catalytic activity, propylene was polymerized for 30 and 60 min by using complexes **1**, **2**, **4** and **5** as catalysts in the presence of MAO (Fig. 3). An obvious decrease in dimerization activity was observed for all four complexes with the prolongation of reaction time, indicating that the active species of these complexes could not steadily survive for a relative long time at high temperature. Moreover, the monomer pressure and the Al/Zr ratio also significantly influenced the catalytic activities of complexes

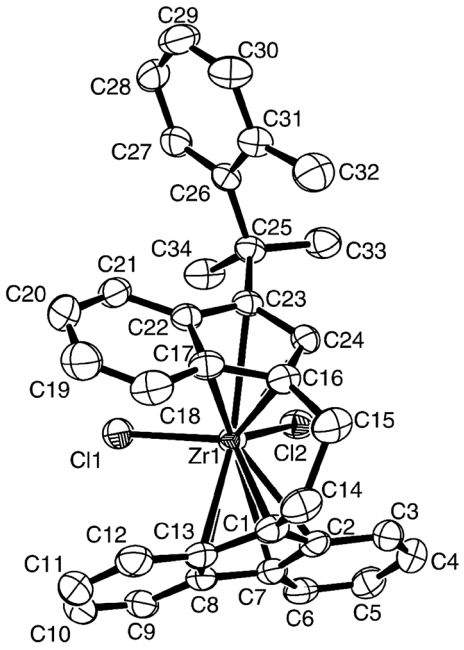


Figure 1. ORTEP view of the molecular structure of complex **4**; hydrogen atoms have been omitted. Selected bond lengths (Å): Zr—C1 = 2.427(2), Zr—C2 = 2.559(2), Zr—C7 = 2.700(2), Zr—C8 = 2.701(2), Zr—C13 = 2.580(2).

Table 1. Dimerization of propylene by complexes **1–9**/MAO[a]

Run	Cat.	P_{PE} (bar)	Time (min)	Yield[b] (mg)	Activity[c] 10^4 g (mol-Zr·h)$^{-1}$	Selectivity (%)[d]	
						2-Methyl-1-pentene	4-Methyl-2-pentene
1	**1**	3	30	13.0	2.08	96.9	3.1
2		6	30	24.1	3.86	96.7	3.3
3	**2**	3	30	20.8	3.33	96.6	3.4
4		6	30	37.2	5.95	97.6	2.4
5	**3**	6	30	Trace	—	—	—
6	**4**	3	30	26.5	4.24	97.7	2.3
7		6	30	44.1	7.06	97.3	2.7
8		6	60	65.5	5.24	95.7	4.3
9[e]		6	30	49.3	7.89	97.6	2.4
10	**5**	3	30	12.5	2.00	97.6	2.4
11		6	30	31.1	4.98	98.4	1.6
12	**6**	6	30	Trace	—	—	—

[a]Conditions: V = 25 ml, [Cat.] = 0.05 mmol l^{-1}, Al/Zr = 4000, 30 min, 100°C.
[b]Measured by GC, the total mass of dimeric products.
[c]Catalytic activity based on all dimeric products.
[d]Percentage in all oligomeric products.
[e]Al/Zr = 8000.

1, **2**, **4** and **5**. With the increase of propylene pressure, the activities of these four complexes were nearly doubled. Increasing the Al/Zr ratio to 8000, the activity of these complexes also increased. However, as depicted in Figs 4–6, the monomer pressure, polymerization time and Al/Zr ratio had a negligible effect on the selectivity of complexes **1**, **2**, **4** and **5** towards propylene dimerization, and high selectivities were obtained in all cases. Noticeably, for all of these zirconocenes, no observable product including 2-methyl-1-pentene could be detected when the polymerization temperature was lower than 100°C.

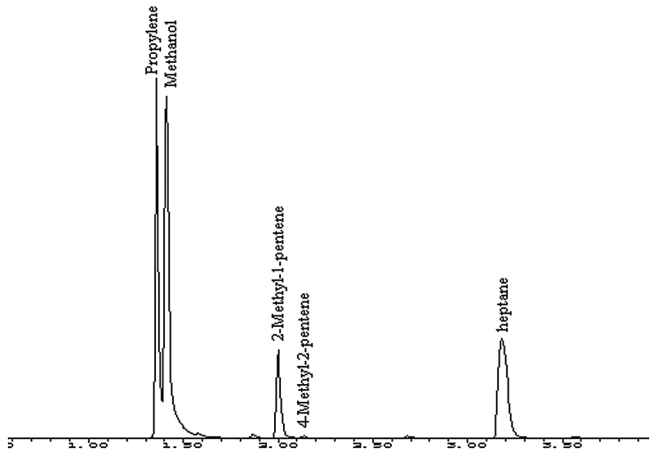


Figure 2. GC trace of propylene dimer made by complex **4**/MAO (run 9).

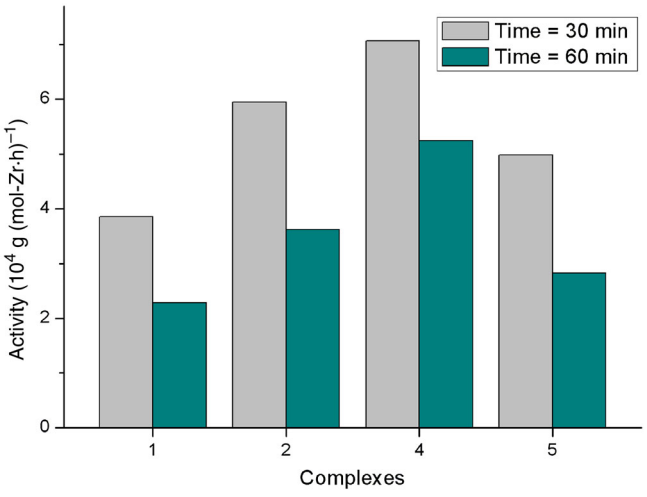


Figure 3. Influence of dimerization time on activity (polymerization conditions: V = 25 ml, [Cat.] = 0.05 mmol l^{-1}, Al/Zr = 4000, 6 bar propylene, 100°C).

Previously, it was reported that *ansa*-zirconocene complexes with a steric bulky substituent at the 3-position of indenyl or cyclopentadienyl ring, such as {C_2H_4—1-[9-$C_{13}H_8$] —2-[1-(3-^{t}Bu)C_9H_5]}$ZrCl_2$,[18c] {Me_2C— [3-(2-CH_3—2-adamantyl)C_5H_3] ($C_{13}H_8$)}$ZrCl_2$,[18e] could polymerize propylene to high-molecular-weight polymers. Thus it is conceivable that the steric bulkiness of the substituent at the 3-position of the indenyl ring in complexes **1**, **2**, **4** and **5** might not be the key factor governing the dimerization activity and selectivity. A similar type of substituents was used to obtain half-sandwich titanium complexes, represented by [(C_6H_5)C(CH_3)$_2$(C_5H_4)]$TiCl_3$, which proved to be highly selective for ethylene trimerization.[21,22] Based on an extensive NMR spectroscopic and DFT (density functional theory) study, Hessen *et al.*[21] suggested that a hemilabile coordination effect of the pendant aryl group to the titanium center was responsible for the trimerization selectivity, and the alkyl groups on the quaternary carbon bridge exerted a crucial influence on the intensity of this hemilabile interaction. Moreover, Green *et al.*[23] proved that a coordination effect (more possibly, an agostic effect) between the pendant phenyl ring and the metal center does exist in the cationic species generated from a

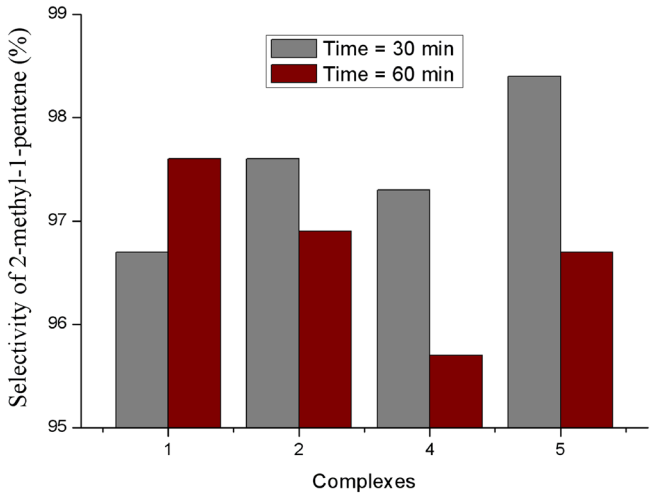


Figure 4. Influence of dimerization time on selectivity (polymerization conditions: $V = 25$ ml, [Cat.] = 0.05 mmol l^{-1}, Al/Zr = 4000, 6 bar propylene, 100°C).

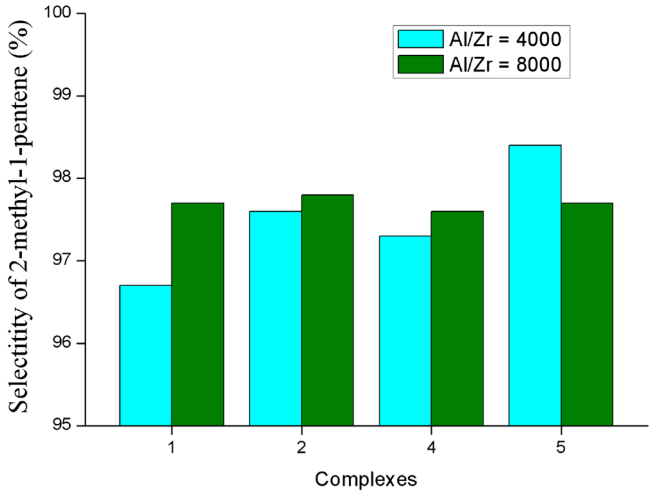


Figure 5. Influence of Al/Zr ratio on selectivity (polymerization conditions: $V = 25$ ml, [Cat.] = 0.05 mmol l^{-1}, 6 bar propylene, 30 min, 100°C).

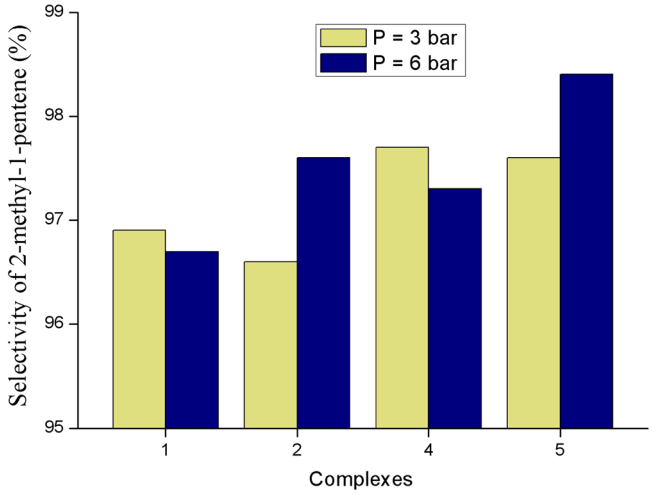
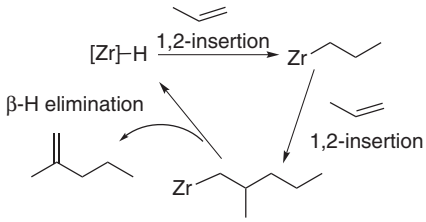


Figure 6. Influence of propylene pressure on selectivity (polymerization conditions: $V = 25$ ml, [Cat.] = 0.05 mmol l^{-1}, Al/Zr = 4000, 6 bar propylene, 100°C).



Scheme 2. Formation of 2-methyl-1-pentene.

16-electron zirconocene complex. All these encourage us to suspect that a similar interaction caused the dimerization of propylene rather than polymerization in this work.

Consistent with this assumption, the introduction of a pendant phenyl group in complex **1** led to a highly selective catalyst for propylene dimerization, while {C_2H_4—1-[9-$C_{13}H_8$] —2-[1-(3-^{t}Bu)C_9H_5]}$ZrCl_2$ with a ^{t}Bu substituent instead of a cumyl group at the 3-position of indenyl ring displayed high isoselectivity and activity for propylene polymerization.[18c] Furthermore, {Ph_2C(9-$C_{13}H_8$)[1-(3-cumyl)C_5H_3]}$ZrCl_2$ bearing the same pendant substituent as complex **1** could not promote propylene polymerization.[24] All these facts evidenced the crucial influence of the pendant aryl group on the catalytic performance.

As suggested by Hessen *et al.*,[21] the alkyl substituents on the quaternary carbon bridge would force the pendant aryl group too close to the metal center, facilitating the occurrence of a hemilabile interaction in the active species. The easy formation of the zircoxacyclic complex **9** with two ethyl groups on the carbon bridge evidenced such a tendency. The negligible activity of complexes **3** and **6** also indicated that the bulkier ethyl groups might make the pendant phenyl ring get much closer to the metal center than the others, which might disturb the coordination of propylene monomer to the active sites. At the present stage, although a hemilabile interaction is still uncertain, the steric hindrance caused by a favorable orientation of the pendant aryl group might be tentatively suggested to be responsible for the dimerization selectivity: after two sequential monomer insertions, the repulsion between the growing chain and surroundings might lead to a chain termination exclusively and thus avoid the formation of trimers and any other longer-chain products. The overwhelming 2-methyl-1-pentene fraction demonstrated that two successive 1,2-insertions followed by a β-hydrogen elimination constituted the dominant pathway in propylene dimerization catalyzed by these complexes and MAO (Scheme 2).[13]

Conclusions

In summary, a series of C_1-symmetric zirconocene complexes with a pendant aryl group on the indenyl ring were synthesized. Among them, complexes **1**, **2**, **4** and **5** with less steric bulky substituents on the carbon bridge could serve as efficient catalysts for propylene dimerization to produce 2-methyl-1-pentene in high selectivity and moderate activity. The steric hindrance around the metal center caused by the adjacency of the pendant aryl group and a possible electronic interaction between this aryl group and the metal center were both supposed to be the factors accounting for propylene dimerization. Our subsequent work will try to develop a comprehensive understanding of the dimerization mechanism operating in these systems.

Acknowledgments

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Supporting Information

Additional supporting information may be found in the online version of this article at the publisher's web-site.

CCDC reference number 959473 for 4. CIF file for 4. Full experimental details, representative NMR spectra of complexes and GC traces of dimeric products are available as ESI. See DOI: 10.1039/b000000x/.