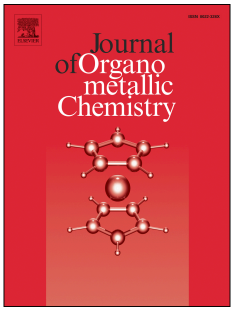

Trinuclear tris(*ansa*-metallocene) complexes of zirconium and hafnium for olefin polymerization

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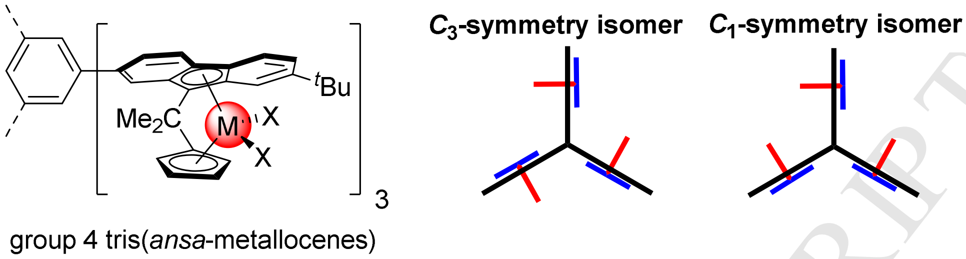


Trinuclear group 4 tris(*ansa*-metallocene) complexes based on an original 1,3,5-phenylene-tris(isopropylidene-bridged cyclopentadienyl/fluorenyl) platform were synthesized and used as precatalysts in polymerization of ethylene and propylene and ethylene/1-hexene copolymerization.

Keywords: *ansa*-metallocene; trinuclear complexes; olefin polymerization; zirconium

Trinuclear Tris(*ansa*-metallocene) complexes of Zirconium and Hafnium for Olefin Polymerization

Lars N. Jende,[1] Aurelien Vantomme,[2] Alexandre Welle,[2] Jean-Michel Brusson,[3] Jean-François Carpentier,[1,]* and Evgueni Kirillov[1,]*

[1] *Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes), UMR 6226, F-35000 Rennes, France.* Corresponding authors: Fax: (+33)(0)223-236-939. E-mail: jean-francois.carpentier@univ-rennes1.fr; evgueni.kirillov@univ-rennes1.fr

[2] *Total Research and Technology Feluy, Zone Industrielle C, B-7181 Feluy, Belgium*

[3] *Total S.A., Direction scientifique, 24 Cours Michelet, F-92069 Paris La Défense, France*

Abstract

New platforms for trinuclear complexes, 1,3,5-tris(fluoren-2-yl-R)benzene (Ph{2-Flu^{R}H}$_3$; R = H (**2a**), 6-^{t}Bu (**2b**), 7-^{t}Bu (**2c**), Tet (**2d**) (Tet = 2,2,5,5-tetramethyl-tetrahydrobenzofluorene), were synthesized via an acid-catalyzed cyclotrimerization of the corresponding substituted 2-acetylfluorenes. Subsequent nucleophilic addition of the [Ph{2-Flu^R}$_3$]$^{3-}$ trianions onto 6,6,-dimethylfulvene afforded the corresponding isopropylidene-bridged pro-ligands Ph{Me$_2$C(2-Flu^{R}H)(C$_5$H$_5$)}$_3$ (**3a-d**). Discrete trinuclear tris(dichloro-*ansa*-zirconocene and hafnocene), Ph[{Me$_2$C(2-Flu^R)(C$_5$H$_4$)}MX$_2$]$_3$ (X = Cl: **4b-d-Zr**, **4c,d-Hf**) were prepared by salt metathesis reactions. Some zirconium complexes were further alkylated towards the corresponding tris(dialkyls) (X = Me: **5c,d-Zr**; X = CH$_2$SiMe$_3$: **6c-Zr**). The structures of

these metal complexes were determined by elemental analyses, and by 1D, inverse 2D heteronuclear correlation, and DOSY NMR spectroscopy, as well as by theoretical computations. Those studies revealed the existence of two isomers, of C_3 and C_1 symmetry respectively, originating from the mutual orientation of the three *ansa*-metallocene fragments. Preliminary studies on the catalytic performances of the dichloro complexes, upon activation with MAO, in ethylene and propylene homopolymerization and ethylene/1-hexene copolymerization were carried out and compared to those of the monometallic analogues under identical conditions.

Introduction

The development of unique, more efficient catalytic systems for olefin polymerization processes has impelled to a rapid progress in the design and synthesis of a variety of dinuclear metallocene compounds, which contain two linked metallocene units.[1] Thereby, a particular emphasis is given to exploration, fundamental understanding and utilization of cooperative interactions (electronic and chemical) between the two proximal metal centers.

Many of the reported dinuclear group 4 metal pre-catalysts for olefin polymerization are based on a homobimetallic platform (Chart 1): (**A**) non-bridged metallocene units connected by hydrocarbon-[2] or silyl/silyloxane-[2e,3] bridges at cyclopentadienyl (Cp) moieties; (**B**) “constrained-geometry systems” linked at the Cp/Ind (Ind = indenyl) moieties or at the si1ylene-bridge;[3d,4] and (**C**) dinuclear bis(*ansa*-metallocenes) linked at the Cp moieties[5] or at the C1/Si1-bridge,[6] respectively.

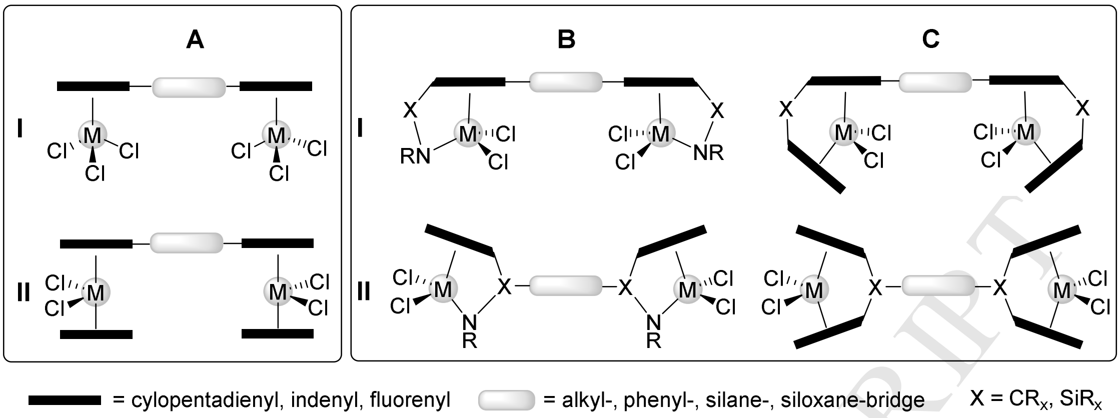


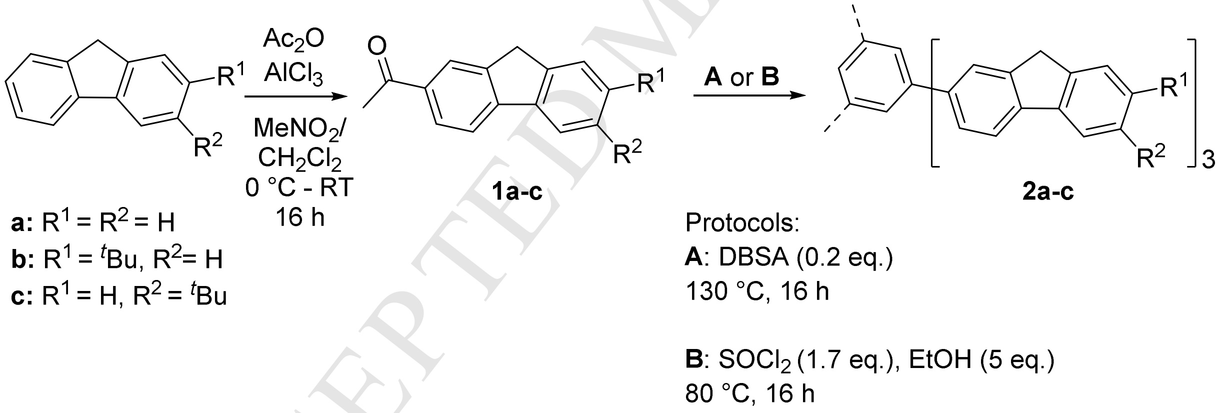
Chart 1. Schematic drawing of common bimetallic platforms encountered in dinuclear group 4 metal pre-catalysts.

To our knowledge, dinuclear bis(metallocene) systems incorporating fluorenyl (Flu) ligands are represented by a sole example, namely $CpZrCl_2((9\text{-}Flu)CH_2CH{=}CHCH_2(9\text{-}Flu))ZrCpCl_2$ (Chart 1, **A II**), which was obtained by a cross-metathesis reaction.[2f, 7] No significant differences between the catalytic performances of the latter dinuclear system and its monometallic analogue have been observed in homopolymerization of ethylene and propylene.

The aim of the investigation reported herein was the synthesis and characterization of a new type of tris(Cp/Flu) pro-ligands based on a 1,3,5-tris(fluoren-2-yl)benzene platform and of some group 4 trinuclear tris(*ansa*-metallocene) complexes derived thereof. The catalytic performances of the synthesized complexes, after activation with MAO, have been investigated in homogeneous polymerization of ethylene and propylene and ethylene/1-hexene copolymerization and compared to those of the mononuclear *ansa*-metallocene reference.

Results and Discussion

Synthesis of 1,3,5-tris(fluoren-2-yl)benzene precursors. Adapting the synthetic procedure described for 1,3,5-tris(fluoren-2-yl)benzene (Ph(2-FluH)$_3$, **2a**), [8] the substituted analogues **2b** and **2c** were synthesized by a 4-dodecylbenzenesulfonic acid (DBSA)-catalyzed cyclocondensation of the corresponding 2-acetylfluorene derivatives (**1b** and **1c**, respectively) under solvent-free conditions (Scheme 1, protocol **A**). However, the products were isolated as deep red solids, suggesting the presence of products resulting from incomplete condensation. Switching the reaction conditions to PTSA-catalyzed cyclotrimerization in toluene solution did not hamper the formation of the red-coloured side-products. Gratifyingly, the use of thionyl chloride as catalyst (Scheme 1, protocol **B**) [9] resulted in the isolation of analytically pure, colorless compounds **2a–c** in good yields (52–55%).



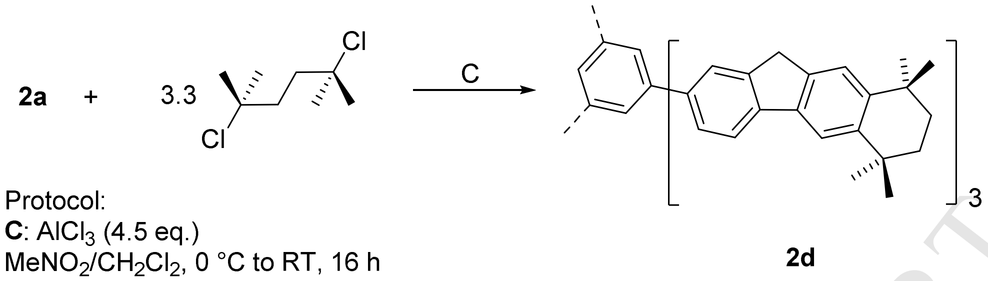
a: $R^1 = R^2 = H$
b: $R^1 = {}^tBu$, $R^2 = H$
c: $R^1 = H$, $R^2 = {}^tBu$

Protocols:
A: DBSA (0.2 eq.)
130 °C, 16 h

B: $SOCl_2$ (1.7 eq.), EtOH (5 eq.)
80 °C, 16 h

Scheme 1. Synthesis of substituted 2-acetylfluorene and corresponding 1,3,5-tri(fluoren-2-yl)benzene derivatives.

A structural analogue, 1,3,5-tris(2-Flu^{Tet})-benzene (**2d**, Tet = 2,2,5,5-tetramethyl-tetrahydrobenzofluorene), was obtained via an improved Friedel-Crafts cycloalkylation of the unsubstituted precursor **2a** with 2,5-dimethyl-2,5-dichlorohexane (Scheme 2, protocol **C**).[10]



Scheme 2. Synthesis of 1,3,5-Ph(2-Flu^{Tet}H)$_3$ (**2d**) *via* Friedel-Crafts cycloalkylation.

The unsubstituted and highly aromatic compound **2a** exhibited poor solubility in most organic solvents (e.g., diethyl ether, dichloromethane, aliphatic or aromatic hydrocarbons), which apparently stems from π-interactions. On the other hand, the substituted products **2b–d** were found readily soluble in the previous solvents. Single crystals of **2c** suitable for X-ray diffraction analysis (Figure 1) were grown by slow evaporation of a dichloromethane/petroleum ether solution at ambient temperature.

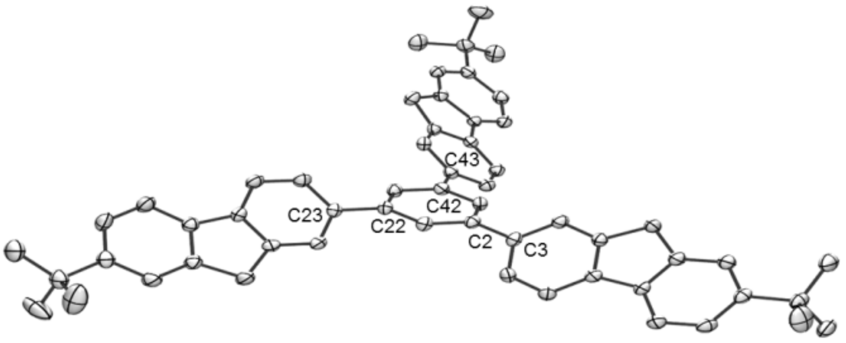
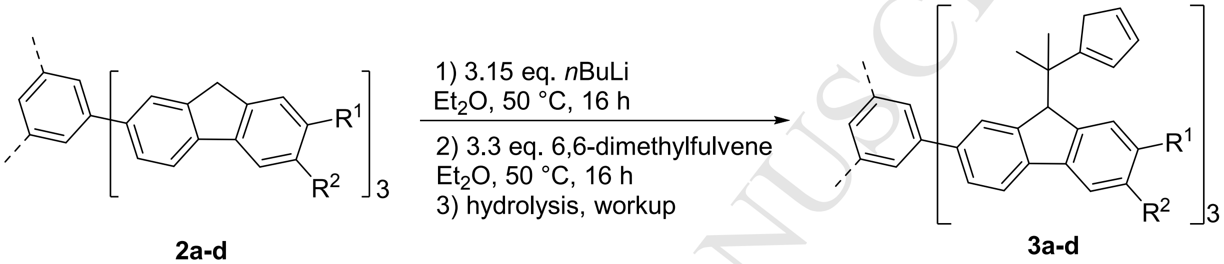


Figure 1. Molecular structure of 1,3,5-Ph(2-{7-^{t}Bu-FluH})$_3$ (**2c**) (atomic displacement parameters are set at the 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths (Å): C2–C3, 1.485(2), C22–C23, 1.485(2), C42–C43, 1.491(2).

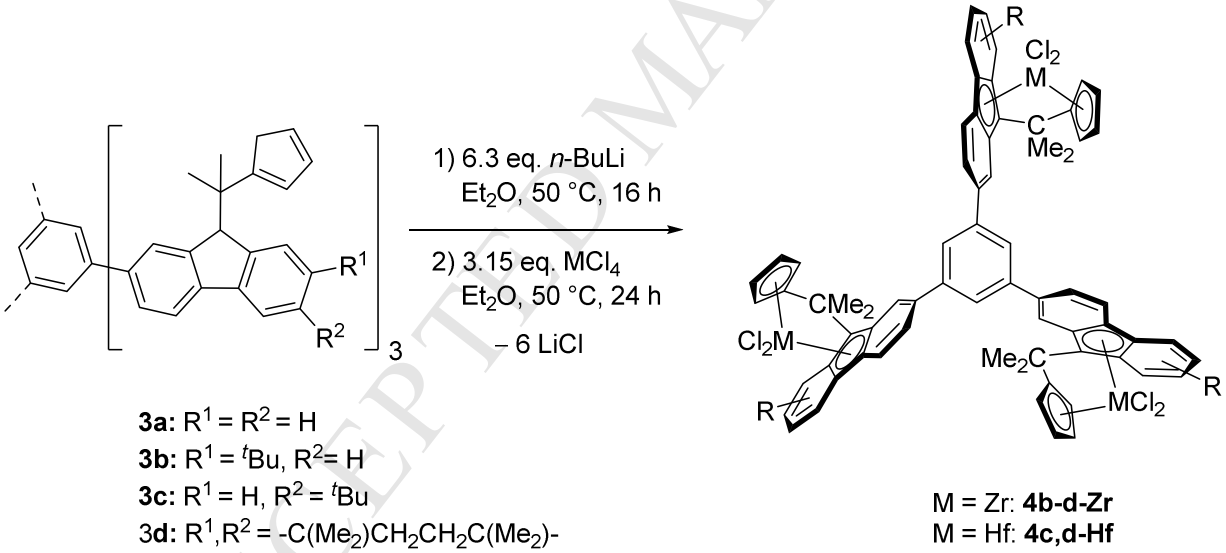
Synthesis of 1,3,5-Ph{$Me_2C(2\text{-}Flu^RH)(C_5H_5)\}_3$ Proligands. The synthesis of monocarbon-bridged fluorenyl-cyclopentadienyl proligands by nucleophilic addition of Cp-type anions onto fulvenes is a well-established reaction.[11] Following this pathway, reaction of the in situ generated $[Ph\{Flu^R\}_3]^{3-}$ anions [(**2a–d**)]$^{3-}$ with 3.3 equiv of 6,6´-dimethylfulvene in diethyl ether and subsequent hydrolysis afforded the desired proligands $Ph\{Me_2C(2\text{-}Flu^RH)(C_5H_5)\}_3$ (**3a–d**) (Scheme 3) in moderate to good yields (29–74%).



Scheme 3. Synthesis of $Ph\{Me_2C(Flu^RH)(C_5H_5)\}_3$ proligands **3a-d**.

At least two isomers, originating from tautomerism within the cyclopentadienyl moieties, were observed for each of the proligands **3a–d** by NMR spectroscopy. The poor solubility of the unsubstituted proligand **3a** hindered its characterization by ^{13}C NMR spectroscopy. For proligands **3b-d**, all signals in the corresponding ^1H and ^{13}C NMR spectra were confidently assigned. In particular, the resonances for the two CH_2 cyclopentadienyl protons appeared at δ 3.1–3.3 ppm and the single resonance for the 9-C*H* proton was observed in the region of δ 4.2–4.4 ppm in the corresponding ^1H NMR spectra (Fig. S15, S17 and S19 for **3b**, **3c** and **3d**, respectively).

Syntheses of tris(dichloro-*ansa*-metallocene) complexes. The synthesis of trinuclear metallocene complexes of zirconium and hafnium derived from the $Ph\{Me_2C(2\text{-}Flu^RH)(C_5H_5)\}_3$ platforms was performed using a standard salt-metathesis reaction between the ligand hexaanions prepared *in situ* in diethyl ether and the corresponding MCl_4 salt (M = Zr, Hf) (Scheme 4). The typical color change of the suspension reactions from reddish-brown (hexaanions) to pink in the case of zirconium and orange-yellow in the case of hafnium metal centers indicated the formation of *ansa*-metallocene complexes in all cases. Extraction of the colored crude solids with dichloromethane allowed isolating analytically pure complexes $Ph(\{Me_2C(2\text{-}Flu^R)(C_5H_4)\}MCl_2)_3$ of zirconium (R = 6-^{t}Bu (**4b-Zr**), 7-^{t}Bu (**4c-Zr**), Tet (**4d-Zr**)) and hafnium (R = 7-^{t}Bu (**4c-Hf**), Tet (**4d-Hf**)) in good yields as pink (81-88%) and orange-yellow (56% and 63%) microcrystalline solids, respectively. On the other hand, due to insolubility issues, this procedure failed in the case of the unsubstituted complexes **4a-Zr** and **4a-Hf** as well as for the 6-*tert*-butyl substituted complex of hafnium **4b-Hf**.



Scheme 4. Synthesis of trinuclear tris(dichloro-*ansa*-metallocene) complexes **4b–d-Zr** and **4c,d-Hf**.

All attempts to grow single-crystals suitable for X-ray diffraction analysis of the synthesized tris(dichloro-*ansa*-metallocene) zirconium and hafnium complexes remained unsuccessful so far. The solution structures of these complexes were analyzed by NMR spectroscopy. Good quality NMR spectra with sharp resonances were obtained for zirconium complexes **4b-d-Zr**, while for the hafnium analogues, conclusive NMR data were obtained only for complex **4c-Hf**. In each case, the ^{1}H and ^{13}C NMR spectroscopic data are consistent with the existence of two isomers exhibiting C_3 and C_1 symmetries, respectively, and differing by the respective orientation of the *ansa*-metallocene moieties (Chart 2). For example, in the aromatic region of the ^{1}H NMR spectrum of **4c-Zr** (Fig. S24), several series of multiplets were observed that belong to the Cp moieties (Fig. 2a). These multiplets consist of overlapping quartets whose splitting originates from $^{3}J_{HH}$ coupling among non-equivalent hydrogens belonging to the same Cp ligands of the two isomers.[12] The presence of the two isomers in a ca. 1:1 ratio was suggested from a simulation of this region of the ^{1}H NMR spectrum (Fig. 2b): four quartets at δ 6.23, 6.12, 5.59 and 5.55 ppm from the four nonequivalent Cp hydrogens of the three equivalent *ansa*-metallocene units in the C_3-symmetric isomer, and twelve overlapping quartets at δ 6.23, 6.20, 6.12, 5.61, 5.59 and 5.55 ppm from the twelve nonequivalent Cp hydrogens of the three non-equivalent *ansa*-metallocene units in the C_1-symmetric congener.

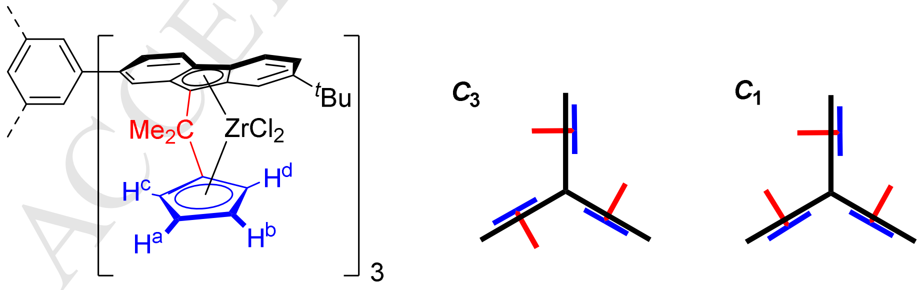


Chart 2. Schematic representation of the C_3- and C_1-symmetric isomers of tris(dichloro-*ansa*-metallocenes) **4b-d-**Zr/Hf.

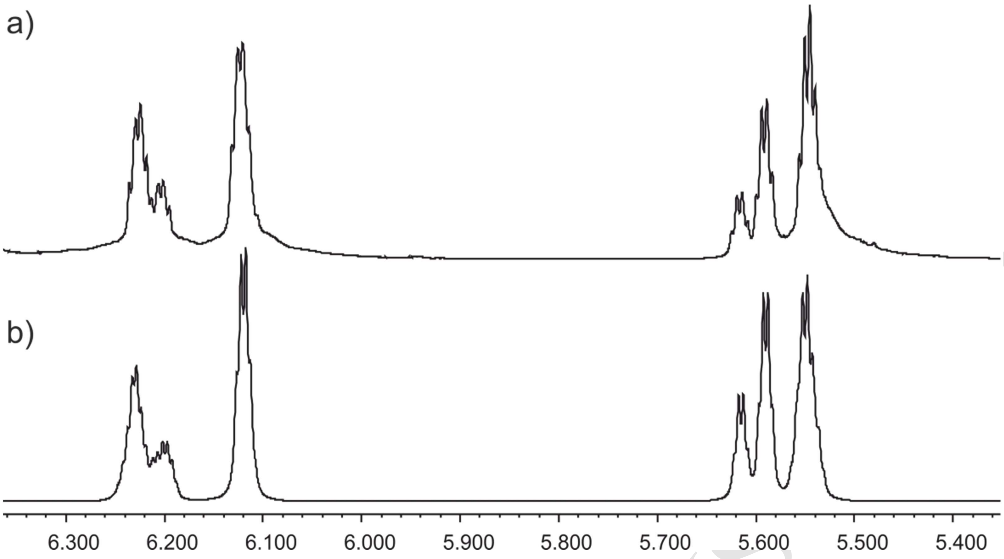


Figure 2. Detailed ^{1}H NMR spectra (Cp region) of complex **4c-Zr**: (a) experimental (500 MHz, C_6D_6, 298 K) and (b) simulated ($^3J_{\text{H-H}}$ = 2.8 Hz).

Possible geometries of the two C_3- and C_1-symmetric isomers of **4c-Zr** were modeled by DFT computations (Fig. 3; see Experimental Section for details). These calculations returned only 1.4 kcal·mol^{-1} of energy difference between the two isomers, which corresponds to a theoretical ratio of ca. 1:10 at room temperature. Note, however, that this minimal energy difference falls within the accuracy of DFT computations usually accepted (2−3 kcal·mol^{-1}) and is therefore not inconsistent with the ca. 1:1 ratio experimentally observed.

Diffusion NMR experiments (PGSE) allowed an estimation of the translation diffusion coefficients D_t for complexes **4b-d-Zr** in benzene-d_6 at room temperature; these were found to fall within a narrow range of 3.6(2)−3.8(2)·10^{-10} m^2·s^{-1}. The corresponding values of the experimental hydrodynamic radii, $r_{\text{H,PGSE}}$ = 8.0−8.1 Å, are in agreement with the DFT computed $r_{\text{H,DFT}}$ values for the isomers of **4c-Zr** of 7.9−8.3 Å.

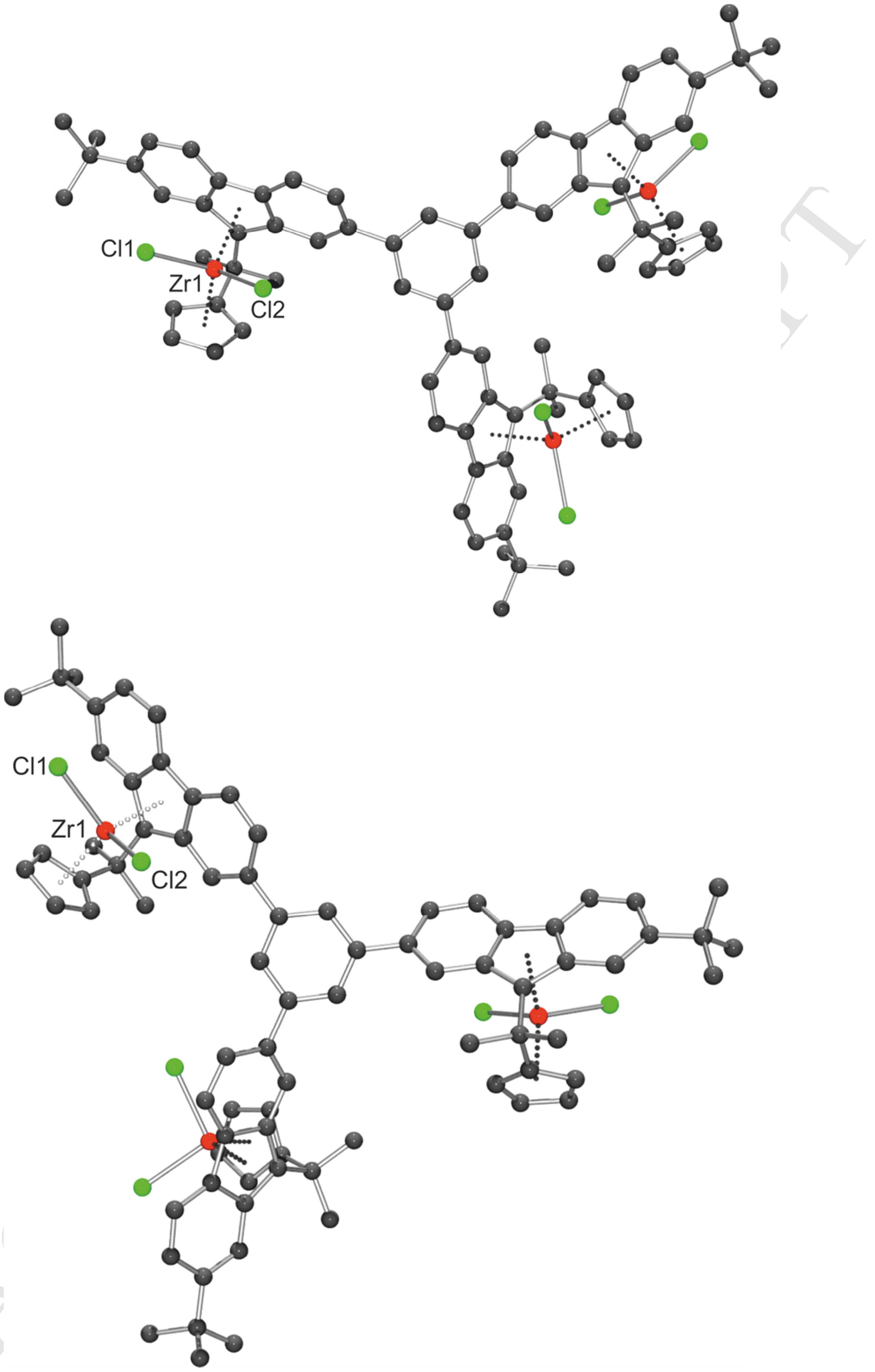
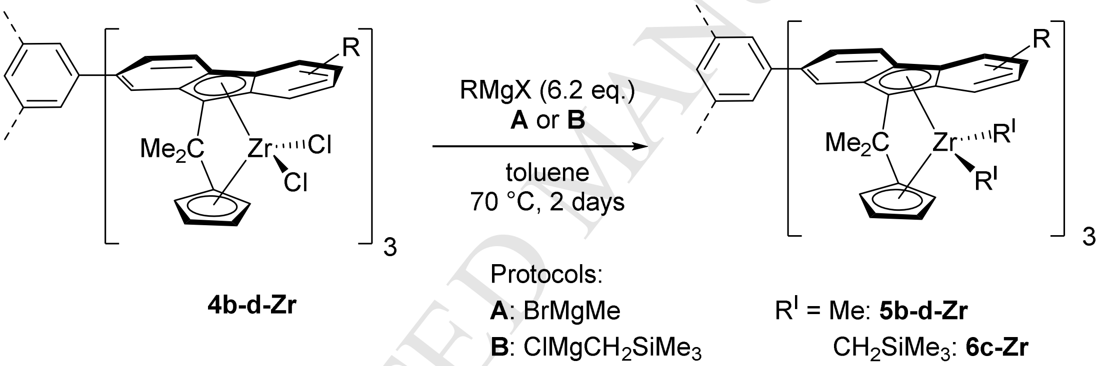


Figure 3. DFT-optimized structures of C_3-symmetric (top) and C_1-symmetric (bottom) isomers of **4c-Zr**.

Syntheses of tris(dialkyl-*ansa*-metallocene) complexes. Aiming at improving the solubility and crystallizability of tris(*ansa*-metallocene) systems, the synthesis of the corresponding alkyls was studied. Following a previously reported protocol,[13] reaction of the parent tris(dichloro-*ansa*-zirconocene) **4c-Zr** and **4d-Zr** with 6 equiv of MeMgBr in toluene yielded after workup the corresponding tris(dimethyl-*ansa*-zirconocene) complexes Ph($\{Me_2C(2\text{-}Flu^R)(C_5H_4)\}ZrMe_2)_3$ **5c-Zr** and **5d-Zr** as yellow solids in 77% and 71% yields (Scheme 5, protocol **A**). Under similar reaction conditions, the treatment of **4c-Zr** with Me_3SiCH_2MgCl afforded the corresponding tris(dialkyl) complex Ph($\{Me_2C(2\text{-}Flu^R)(C_5H_4)\}Zr(CH_2SiMe)_2)_3$ (**6c-Zr**) as a yellow-orange solid in 80% yield (Scheme 5, protocol **B**).[14]



Scheme 5. Alkylation of tris(dichloro-*ansa*-zirconocenes) **4b-d-Zr** with Grignard reagents.

Although the tris(dialkyl) complexes **5c,d-Zr** and **6d-Zr** showed good solubility in aliphatic (hexane, heptane) and aromatic (benzene, toluene) hydrocarbons, all crystallization attempts systematically returned microcrystalline precipitates which proved unsuitable for single-crystal X-ray diffraction studies.[15] Nevertheless, the recorded NMR spectroscopic data for the tris(dimethyl) **5c,d-Zr** and tris(bis(trimethylsilyl)) **6c-Zr** complexes proved informative (see SI). While the chemical shifts for the aromatic hydrogens of the Ph($\{Me_2C(2\text{-}Flu^R)(C_5H_4)\}_3$ ligand system barely remained unchanged in the corresponding ^{1}H NMR spectra in all cases (Fig. S32, S35 and S38, respectively), two groups of broad signals of equal intensity for several isochronous hydrogens of the six methyl groups (δ **5c-Zr**: −0.92 and −1.08 ppm, **5d-Zr**: −0.92 and −1.15 ppm, respectively), observed at high field, are in agreement with complete Cl→Me exchange. Also, the ^{13}C NMR signals for the Zr−CH_3 groups were found in the range of δ 33.5 to 32.1 ppm for both complexes, as assigned by HSQC NMR spectroscopy (Fig. S34 and S36, respectively). On the other hand, the presence of the two C_3- and C_1-symmetric isomeric forms of **5c-Zr** and **5d-Zr** could not be unequivocally established, due to presumably close magnetic equivalence of the respective nuclei.

For the tris(bis(trimethylsilyl)) complex **6c**-Zr, the ^{1}H NMR signals from the $SiMe_3$ groups were observed in the region δ 0.14 to −0.01 ppm (Fig. S38). The four overlapping multiplets at δ −0.94, −1.49, −1.91 and −2.06 ppm were assigned to the diastereotopic methylenic hydrogens from six Zr−(CH_2Si{CH_3}$_3$)$_2$ units. In the HSQC spectrum of **6c-Zr** (Fig. S40), the ^{13}C NMR signals from several isochronous CH_2 groups appeared at δ 50.4, 48.6, 45.2, and 44.9 ppm; the signals from the four different SiCH_3 carbons were found between δ 2.8 ppm and 3.4 ppm in the HMBC NMR spectrum (Fig. S41). These observations clearly evidence the coexistence of two isomers in **6c**-Zr.

Polymerization Studies. The tris(dichloro-*ansa*-zirconocenes) **4b−d-Zr**, in combination with MAO, were studied in homogeneous polymerization of ethylene and propylene and in ethylene/1-hexene copolymerization (toluene solution, 5 bar constant pressure, T_{pol} = 20 °C and 60 °C).[16] For comparison purposes, the catalytic performance of the monometallic reference metallocene catalysts {$Me_2C(Flu)(C_5H_4)$}$ZrCl_2$ (**M1**) and {$Me_2C(2,7\text{-}^{t}Bu_2Flu)(C_5H_4)$}$ZrCl_2$ (**M2**) were determined under identical conditions. Selected polymerization data are summarized in Tables 1−3.

In homopolymerization of ethylene at 20 and 60 °C (Table 1), both mono- and tris-(*ansa*-zirconocene) catalysts exhibited quite similar outcome in terms of productivity (compare e.g. entries 1, 3 *vs* 5, 7, 9 and 2, 4 *vs* 6, 8, 10). All the recovered PEs featured melting (T_m) and crystallization (T_c) transitions in a narrow temperature range (132.0−136.4 °C and 117.2−118.1 °C, respectively). The only significant difference observed is a *ca*. 2-fold increase of the molecular weight (M_n) of polymers obtained with **4b,c,d-Zr** with respect to those obtained with their mononuclear analogues (compare entries 6, 8, 10 *vs* 2, 4, respectively). This may reflect a moderate propensity of the tris(*ansa*-zirconocene) systems to influence positively chain growth due to putative cooperative effects.

Table 1. Ethylene Homopolymerization. [a]

Run	Precatalyst	[Zr] [μmol·L^{-1}]	T_{pol} [°C]	m$_{pol}$ [g]	Productivity [kg·mol^{-1}·h^{-1}]	T_m^{c} [°C]	T_c^{c} [°C]	M_n^{d} (× 10^3) [g·mol^{-1}]	M_w/M_n^{d}
1[b]	**M1**	30	20	3.22	4,290	135.1	117.9	n.d.	n.d.
2	**M1**	10	60	2.66	7,090	135.1	117.9	25.7	3.5
3	**M2**	10	20	0.69	1,820	133.1	n.d.	115.5	4.1
4	**M2**	10	60	2.79	7,370	132.0	n.d.	39.4	3.9
5	**4b-Zr**	30	20	1.61	4,290	135.9	117.4	n.d.	n.d.
6	**4b-Zr**	10	60	2.21	5,890	134.9	117.2	70.7	5.5
7	**4c-Zr**	30	20	1.41	3,760	135.6	117.9	n.d.	n.d.
8	**4c-Zr**	10	60	1.72	4,590	134.3	118.1	67.8	4.6
9	**4d-Zr**	30	20	1.65	4,400	136.4	117.6	n.d.	n.d.
10	**4d-Zr**	10	60	1.54	4,110	135.5	117.4	64.2	4.5

[a] Polymerization conditions: 300 mL high-pressure glass reactor; solvent: toluene, 150 mL; P[ethylene] = 5 bar (constant); $[MAO]_0/[Zr]_0$ = 5,000; t = 15 min. [b] t = 30 min. [c] Determined by DSC from second run. [d] Determined by GPC.

Homopolymerization of propylene with the investigated catalytic systems afforded syndiotactic and syndiotactic-enriched polypropylenes (Table 2). In that case, the tris(*ansa*-zirconocene) systems appeared to be significantly less productive than the reference catalysts **M1** and **M2**, both at 20 °C and 60 °C (compare entries 1, 3 *vs* 5, 7, 9 and 2, 4 *vs* 6, 8, 10). Also, a lesser stereoselective character of **4b,c,d-Zr** is evidenced from a lower content of syndiotactic pentads ($[r]^4$ = 60−64 % at 60 °C and 77−78 % at 20 °C) than those of the mononuclear analogue **M2** ($[r]^4$ = 74.7 % at 60 °C and 89.0 % at 20 °C). This was also noticed in the T_m/T_c values.[17] As for the homopolymerization of ethylene, the nuclearity of catalysts did not affect substantially the molecular weights (M_n) and polydispersities; for both mono- and tris(*ansa*-metallocene) systems, the M_w/M_n values were found in a narrow range ($Đ_M$ = 2.2−3.6).

Table 2. Propylene Homopolymerization. [a]

Run	Prec.	[M] [µmol·L^{-1}]	T_{pol} [°C]	m_{pol} [g]	Prod. [kg·mol^{-1}·h^{-1}]	T_m[c] [°C][17]	T_c[c] [°C]	M_n[d] ($\times 10^3$) [g·mol^{-1}]	M_w/M_n[d]	[*rrrr*] [%][e]
1[b]	**M1**	30	20	25.7	5,710	122.1 134.5	83.6	27.0	2.7	79.3
2	**M1**	10	60	3.45	4,550	113.1	55.5	13.2	3.6	64.2
3	**M2**	10	20	6.32	8,340	141.5 150.5	97.9	35.5	2.2	89.0
4	**M2**	10	60	19.6	25,870	111.7 119.0	51.1	16.8	2.2	74.7
5	**4b-Zr**	30	20	2.01	890	126.8 140.2	90.9	18.8	3.0	77.3
6	**4b-Zr**	10	60	0.96	1,280	93.2 113.9	n.d.	13.2	2.7	61.1
7	**4c-Zr**	30	20	1.51	670	128.0 140.3	90.3	25.0	3.2	78.5
8	**4c-Zr**	10	60	0.76	1,010	96.9 115.9	n.d.	13.4	2.6	60.2
9	**4d-Zr**	30	20	1.70	760	126.6 140.2	88.6	22.2	3.4	78.0
10	**4d-Zr**	10	60	0.97	1,290	109.9	n.d.	13.2	2.7	64.1

[a] Polymerization conditions: 300 mL high-pressure glass reactor; solvent: toluene, 150 mL; p[propylene] = 5 bar (constant); $[MAO]_0/[Zr]_0$ = 5,000; t = 30 min. [b] t = 60 min. [c] Determined by DSC from second run. [d] Determined by GPC. [e] Determined by ^{13}C NMR spectroscopy.

In ethylene/1-hexene copolymerization (Table 3), a drop in productivity was observed for the tris(*ansa*-metallocene) systems **4b-Zr** and **4d-Zr** (entries 3−6) as compared to the mononuclear **M2**. Also, both catalysts enabled a lower incorporation of 1-hexene than the reference system **M2** (entries 1 and 2) and, therefore, the resulting copolymers exhibited higher T_m values.

Table 3. Ethylene/1-hexene Copolymerization.[a]

Run	Prec.	[M] [µmol·L^{-1}]	T [°C]	m_poly [g]	Prod. [kg·mol^{-1}·h^{-1}]	T_m[b] [°C]	M_n[c] (× 10^3) [g·mol^{-1}]	$M_\mathrm{w}/M_\mathrm{n}$[c]	C_6 [%][d]	
									mol.	wt.
1	**M2**	30	20	2.23	980	97.9	70.1	2.7	4.6	12.6
2	**M2**	10	60	8.89	23,470	82.3	29.7	2.4	6.8	17.9
3	**4b-Zr**	30	20	3.61	1,590	100.8 122.8	n.d	n.d	2.6	7.5
4	**4b-Zr**	10	60	4.24	11,190	100.0 123.4	37.5	3.7	2.0	5.8
5	**4d-Zr**	30	20	1.54	680	124.9	n.d	n.d	0.8	2.4
6	**4d-Zr**	10	60	1.53	4,040	125.9	31.0	5.6	0.7	2.0

[a] Polymerization conditions: 300 mL-high pressure glass reactor; solvent: toluene, 150 mL; p[ethylene] = 5 bar; [MAO]/[Zr] = 5,000; t = 15 min; [1-hexene]$_0$ = 0.02 mol (2.5 mL); [b] Determined by DSC from second run. [c] Determined by GPC. [d] Determined by ^{13}C NMR spectroscopy.

Conclusion

A straightforward synthesis of a series of novel arene-linked tris(Cp/Flu) ligand systems was developed. These systems were used for the preparation of trinuclear tris(*ansa*-metallocene) chlorides and alkyls derived thereof. Solution NMR spectroscopy and theoretical computations established that these tris(*ansa*-{Cp/Flu}-metallocene) complexes exist as ca. 1:1 mixtures of isomers featuring overall C_3 and C_1 symmetries.

Ethylene and propylene homopolymerization as well as ethylene/1-hexene copolymerization experiments were conducted using the trinuclear chloride catalyst precursors in combination with MAO. Comparison with experiments performed with mononuclear analogues showed no significant intermetallic cooperativity in the trinuclear systems. Though in ethylene homopolymerization, trinuclear systems behaved equivalently as their mononuclear counterparts in terms of productivity, providing somewhat higher molecular weight homopolymers, a drop in the incorporation comonomer content in ethylene/1-hexene copolymerization was observed with the former precatalysts. Also, the trinuclear systems appeared to be less syndioselective and productive in propylene homopolymerization as compared to the reference mononuclear catalyst. The origin of these discrepancies remained unclear so far. Possibly, the excessive steric hindrance from the bulky MAO anions crowding the trinuclear trication may negatively affect the access of monomer molecules to the active centers, thus hampering propagation (and hence reducing the overall productivity) as well as enantiofacial stereodifferentiation. Further investigations in our laboratories are currently focused on the elaboration of other polynuclear precatalysts with improved performances and identification of the nature of possible intermetallic cooperative effects.

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Experimental section

General Considerations. All manipulations (except polymerizations) were performed under a purified argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents were distilled from Na/benzophenone (THF, Et_2O) and Na/K alloy (toluene, pentane) under argon, degassed thoroughly and stored under argon prior to use. Deuterated solvents (benzene-d_6, toluene-d_8, THF-d_8; >99.5% D, Deutero GmbH and Euroisotop) were vacuum-transferred from Na/K alloy into storage tubes. $CDCl_3$, CD_2Cl_2 and $C_2D_2Cl_4$ were kept over CaH_2 and vacuum-transferred before use. MAO (30 wt-% solution in toluene, Albemarle; contains ca. 10 wt-% of free $AlMe_3$) was used as received. Ligand precursors **a** and **b** were generously provided by Total Petrochemicals. Precursors **c**,[18] **2a**,[8] **M1** and **M2**[19] were prepared according to literature protocols. Other starting materials were purchased from Alfa, Strem, Acros or Aldrich, and used as received.

Instruments and Measurements. NMR spectra of complexes were recorded on Bruker AM-400 and AM-500 spectrometers in Teflon-valved NMR tubes at 25 °C, unless otherwise indicated; chemical shifts are reported in ppm vs $SiMe_4$ using the residual solvent resonances. Assignment of resonances was made from 2D ^1H–^1H COSY, ^1H–^{13}C HSQC and HMBC NMR experiments. Coupling constants are given in Hertz. Elemental analyses (C, H, N) were performed using a Flash EA1112 CHNS Thermo Electron apparatus. DSC measurements were performed on a SETARAM Instrumentation DSC 131 differential scanning calorimeter at heating rate of 10 $°C\cdot min^{-1}$; first and second runs were recorded after cooling to 30 °C; the reported melting and crystallization temperatures correspond to the second run. GPC analyses of polymer samples were carried out in 1,2,4-trichlorobenzene at 135 °C at the Total Petrochemicals research center in Feluy (Belgium), using polystyrene standards for universal calibration. ^{13}C NMR analyses of propylene and copolymer samples were run on a AM-500 Bruker spectrometer (Total Petrochemicals, Feluy, Belgium) as follows: solutions of ca. 200 mg of PP or PEH polymer in trichlorobenzene/C_6D_6 mixture at 135 °C in 10 mm tubes, inverse gated experiment, pulse angle 90°, delay 11 sec, acquisition time 1.25 sec, number of scans 6000.

1-(6-(*Tert*-butyl)-9*H*-fluoren-2-yl)ethanone (1b). At 0 °C, a solution of $AlCl_3$ (2.21 g, 16.5 mmol) in $MeNO_2$ (10 mL) was syringed into a mixture of 3-(*tert*-butyl)-9*H*-fluorene (2.22 g, 10 mmol) and acetic anhydride (1.33 g, 13 mmol) in $MeNO_2$/1,2-dichloroethane (35 + 35 mL). The mixture was stirred for 60 min and poured into a beaker with ice (100 g). The mixture was extracted with hexane (3 × 100 mL). The solvent was evaporated leaving **1b** as a pale yellow solid (2.26 g, 8.5 mmol, 52% yield). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.16 (s, 1H), 8.04 (dt, *J* = 8.0, 1.3 Hz, 1H), 7.92-7.87 (m, 2H), 7.55 (d, *J* = 8.0, 1H), 7.47 (dd, *J* = 8.0, 1.8, 1H), 3.94 (s, 2H, 9-FluH_2), 2.69 (s, 3H, COCH_3), 1.44 (s, 9H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 198.1 (COCH$_3$), 150.4, 146.8, 143.7, 141.8, 140.4, 135.5, 127.7, 125.6, 125.0, 124.8, 119.5, 117.5, 36.5 (9-Flu), 34.9 (C(CH$_3$)$_3$), 31.6 (C(CH$_3$)$_3$), 26.8 (COCH$_3$). Elemental analysis calcd (%) for $C_{19}H_{20}O$ (264.36): C 86.32, H 7.63; found: C 86.50, H 7.77

1-(7-(*Tert*-butyl)-9*H*-fluoren-2-yl)ethanone (1c). Using a procedure similar to that described above for **1b**, compound **1c** was obtained from $AlCl_3$ (2.21 g, 16.5 mmol), 2-(*tert*-butyl)-9*H*-fluorene (**c**) (2.22 g, 10 mmol) and acetic anhydride (1.33 g, 13 mmol) in $MeNO_2$/1,2-dichloroethane (35 + 35 mL). Product **1c** was isolated as a pale yellow solid (2.38 g, 9.0 mmol 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.16 (d, J = 0.9, 1H), 8.02 (dt, J = 8.0, 1.3, 1H), 7.81 (dd, J = 9.6, 8.1, 4H), 7.66 (d, J = 1.0, 1H), 7.49 (dd, J = 8.1, 1.8, 2H), 3.97 (s, 2H, 9-FluH_2), 2.68 (s, 3H, COCH_3), 1.42 (s, 9H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 25 °C) δ = 197.7 (COCH$_3$), 151.6, 146.4, 144.7, 143.5, 137.8, 135.3, 127.6, 124.9, 124.8, 124.3, 122.2, 120.3, 119.3, 36.9 (9-Flu), 34.9 (C(CH$_3$)$_3$), 31.3 (C(CH$_3$)$_3$), 26.6 (COCH$_3$). Elemental analysis calcd (%) for $C_{19}H_{20}O$ (264.36): C 86.32, H 7.63; found: C 86.41, H 7.89.

1,3,5-Tris(6-(*tert*-butyl)-9*H*-fluoren-2-yl)benzene, Ph($^{6\text{-}t\text{Bu}}$FluH$_2$)$_3$ (2b). In a 250 mL flask, **1b** (3.00 g, 11.35 mmol) was suspended in EtOH (3.3 mL). $SOCl_2$ (2.25 g, 3.4 mL, 19 mmol) was added dropwise over a period of about 20 min. The reaction mixture was stirred and gently refluxed for 24 h. After completion of the reaction, the mixture was neutralized by saturated Na_2CO_3. The precipitate was collected by filtration, washed with water, ethanol, and a small amount of ethyl acetate (20 mL) followed by drying in vacuum to yield the almost pure product. The crude product was dissolved in CH_2Cl_2, precipitated by addition of MeOH and dried *in vacuo*. Pure **2b** was isolated as a yellow solid (1.77 g, 2.40 mmol, 63%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7 7.96 (m, 3H), 7.96 (s, 3H, PhH), 7.91 (d, J = 1.8, 3H), 7.81 (dd, J = 8.0, 1.6, 3H), 7.55 (d, J = 8.0, 3H), 7.43 (dd, J = 8.0, 1.8, 3H), 4.00 (s, 6H, 9-FluH_2), 1.48 (s, 27H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 25 °C): δ 150.1, 144.4, 142.7, 141.5, 141.3, 140.7, 139.7, 126.1, 125.0, 124.6, 124.2, 124.0, 120.0, 116.8, 36.6 (9-Flu), 34.9 (*C*(CH_3)$_3$), 31.7 (C(*C*H_3)$_3$). Elemental analysis calcd (%) for $C_{57}H_{54}$ (739,04): C 92.64, H 7.36; found: C 92.64, H 7.62. ASAP-MS (*m/z*): 739.4299 ([M + H]$^+$), 738.422([M]$^+$), 683.3676) [(M - ^{t}Bu + H]$^+$).

1,3,5-Tris(7-(*tert*-butyl)-9*H*-fluoren-2-yl)benzene, Ph($^{7\text{-}t\mathrm{Bu}}$FluH$_2$)$_3$ (2c). Using a procedure similar to that described above for **2b**, compound **2c** was obtained from **1c** (7.60 g, 28.75 mmol) and $SOCl_2$ (5.70 g, 3.4 mL, 48 mmol). The titled compound **2c** was obtained as a yellow solid (6.30 g, 8.50 mmol, 88%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.94 (s, 6H, Ph*H*), 7.88 (d, *J* = 7.9, 3H), 7.79 (d, *J* = 8.1, 3H), 7.78 (dd, *J* = 8.0, 1.5, 3H), 7.65 (d, *J* = 1.7, 3H), 7.49 (dd, *J* = 8.1, 1.8, 3H), 4.02 (s, 6H, 9-Flu*H*$_2$), 1.44 (s, 27H, C(C*H*$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 150.2, 144.1, 143.5, 142.6, 141.2, 139.4, 138.8, 126.2, 124.9, 124.1, 124.0, 122.0, 119.9, 119.5, 37.1 (9-Flu), 34.9 (*C*(CH_3)$_3$), 31.6 (C(*C*H_3)$_3$). Elemental analysis calcd (%) for $C_{57}H_{54}$ (739.04): C 92.64, H 7.36; found: C 92.51, H 7.26. ASAP-MS (*m/z*): 739.429 ([M + H]$^+$), 738.422 ([M]$^+$).

1,3,5-Tris(6,6,9,9-tetramethyl-7,8,9,11-tetrahydro-6*H*-benzo[b]fluoren-2-yl)benzene, Ph($^{\mathrm{Tet}}$FluH$_2$)$_3$ (2d). Using a procedure similar to that described above for **1b**, compound **2d** was obtained from $AlCl_3$ (3.90 g, 29.0 mmol), **2a** (3.15 g, 5.52 mmol), 2,5-dichloro-2,5-dimethylhexane (3.94 g, 21.0 mmol) in a $MeNO_2$/1,2-dichloroethane mixture (80/80 mL). Product **2d** was isolated as a pale yellow solid (2.81 g, 3.10 mmol, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.98 (s, 3H), 7.96 (s, 3H, Ph*H*), 7.93 (d, *J* = 7.9, 3H), 7.86 (s, 3H), 7.81 (d, *J* = 8.1, 3H), 7.61 (s, 3H), 4.01 (s, 6H, 9-Flu*H*$_2$), 1.83 (s, 12H, C*H*$_2$), 1.48 (s, 18H, C(C*H*$_3$)$_2$), 1.43 (s, 18H, C(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 144.2, 144.0, 143.8, 142.7, 141.4, 140.9, 139.5, 139.1, 128.1, 127.8, 127.1, 126.3, 126.1, 125.3, 125.1, 124.9, 124.0, 123.1, 120.9, 119.9, 117.8, 36.7 (9-Flu), 35.4, 35.3 (*C*(CH_3)$_2$), 34.7, 34.6 (*C*H_2*C*H_2), 32.4, 32.2

(C(CH_3)$_2$). Elemental analysis calcd (%) for $C_{69}H_{72}$ (901.31): C 91.95, H 8.05; found: C 91.68, H 7.85. ASAP-MS (*m/z*): 900.563 ([M]$^+$), 790.453 ([M - Me_2CCp]$^+$), 680.343 ([M - (Me_2CCp)$_2$]$^+$), 570.233 ([M - (Me_2CCp)$_3$]$^+$).

1,3,5-Tris(9-(2-(cyclopenta-1,3-dien-1-yl)propan-2-yl)-9*H*-fluoren-2-yl)benzene, Ph{Me_2C(2-FluH)(CpH)}$_3$ (3a). To a solution of 1,3,5-tri(9*H*-fluoren-2-yl)benzene (**2a**) (1.77 g, 3.10 mmol) in dry THF (50 mL) was added dropwise at 0 °C *n*-BuLi (3.7 mL of a 2.5 M solution in hexane, 9.3 mmol) over 15 min. The mixture was stirred at room temperature overnight. Then, 6,6´-dimethylfulvene (0.987 g, 9.30 mmol) was added slowly and the resulting red mixture was stirred at room temperature for 16 h. The mixture was quenched with saturated NH_4Cl solution (40 mL), extracted with diethyl ether (3 × 50 mL), and the combined organic phase was dried over Na_2SO_4/Na_2CO_3. After removal of the solvent, the crude product was dissolved in CH_2Cl_2, precipitated by addition of MeOH under vigorous stirring and dried *in vacuo*. Proligand **3a** was recovered as a pale yellow solid (356 mg, 0.59 mmol, 29%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.91 (m, 3H), 7.85 (s, 3H, Ph*H*), 7.77 (m, 6H), 7.58 (m, 3H), 7.44(m, 3H) (m, 3H), 7.41 (m, 3H), 7.35 (m, 3H), 7.28 (m, 3H), 7.06, 6.69, 6.59, 6.54, 6.26, 6.04 (6m, 9H, Cp*H*), 4.35, 4.32 (2s, 3H, 9-Flu*H*), 3.31, 3.11 (2s, 6H, CpH_2), 1.32, 1.24 (2m, 9H, C(CH_3)$_2$), 1.12, 1.07 (2m, 9H, C(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 146.2, 145.7, 143.7, 142.5, 141.2, 139.8, 132.4, 131.3, 127.2, 126.8, 126.6, 126.2, 126.1, 125.1, 124.7, 124.0, 120.1, 120.0, 119.5 (CpH), 58.0 (9-Flu), 40.6 (CpCH_2), 37.0 (*C*(CH_3)$_2$), 25.6 (C(CH_3)$_2$). Elemental analysis calcd (%) for $C_{69}H_{60}$ (889.21): C 93.20, H 6.80; found: C 93.11, H 6.77. ESI-MS (*m/z*): 911.4596 ([M + Na]$^+$), 805.379 ([(M - Me_2CCp) + Na]$^+$).

1,3,5-Tris(6-(*tert*-butyl)-9-(2-(cyclopenta-1,3-dien-1-yl)propan-2-yl)-9*H*-fluoren-2-yl)benzene, Ph{Me_2C(2-(6-^{tBu}FluH))(CpH)}$_3$ (3b). Using a protocol similar to that described for **3a**, compound **3b** was obtained from **2b** (1.00 g, 1.35 mmol), *n*-BuLi (1.7 mL of a 2.5 M solution in hexane, 4.3 mmol) and 6,6´-dimethylfulvene (0475 g, 4.4 mmol). **3c** was isolated as a pale yellow solid (1.00 g, 0.95 mmol, 71%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.88 (m, 3H), 7.84 (s, 3H, Ph*H*), 7.75 (m, 3H), 7.67 (m, 3H), 7.48-7.35 (m, 6H), 7.23 (m, 3H), 7.02, 6.66, 6.59, 6.51, 6.27, 6.03 (6m, 9H, Cp*H*), 4.26, 4,23 (2s, 3H, 9-Flu*H*), 3.29, 3.09 (2s, 6H, CpH_2), 1.45 (s, 27H, $C(CH_3)_3$), 1.32 (m, 9H, $C(CH_3)_2$), 1.07 (s, 9H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ 158.2 (6-Flu), 150.3, 150.2, 146.4, 142.8, 141.7, 141.5 (Flu), 134.4, 133.3, 132.4, 131.1, 126.6, 125.8 (Flu), 125.6, 125.0, 123.6, 123.5, 119.3, 116.3 (CpH), 57.8, 55.5 (9-Flu), 41.0, 40.8 ($C(CH_3)_2$), 40.6, 39.6 (CpCH_2), 34.8 ($C(CH_3)_3$), 31.7, 31.6 ($C(CH_3)_3$), 27.0, 25.3, 24.3 ($C(CH_3)_2$). Elemental analysis calcd (%) for $C_{81}H_{84}$ (1057.53): C 91.99, H 8.01; found: C 91.71, H 7.79. ESI-MS (*m/z*): 1056.6564 ($[M]^+$), 1079.6461 ($[M + Na]^+$), 1095.6188 ($[M + K]^+$).

1,3,5-Tris(7-(*tert*-butyl)-9-(2-(cyclopenta-1,3-dien-1-yl)propan-2-yl)-9*H*-fluoren-2-yl)benzene, Ph{Me$_2$C(2-(7-^{tBu}FluH))(CpH)}$_3$ (3c). Using a protocol similar to that described for **3a**, compound **3c** was obtained from **2c** (1.42 g, 1.90 mmol), *n*-BuLi (2.4 mL of a 2.5 M solution in hexane, 6.00 mmol) and 6,6´-dimethylfulvene (0.665 g, 6.30 mmol). **3c** was isolated as a pale yellow solid (1.84 g, 1.74 mmol, 92%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.90 (dd, *J* = 7.9, 1.7, 3H), 7.79 (m, 6H), 7.74 (s, 3H, Ph*H*), 7.67, 7.54 (2t, *J* = 2.3, 3H), 7.45 (dt, *J* = 8.2, 2.3, 2H), 7.32, 7.23 (2s, 3H, 9-Flu*H*), 7.08, 6.72, 6.60, 6.56, 6.25, 6.04 (6m, 9H, Cp*H*), 4.33, 4.29 (2s, 3H, Flu*H*), 3.32, 3.13 (2s, 6H, CpH_2), 1.37, 1.36 (2s, 27H, $C(CH_3)_3$), 1.24, 1.22, 1.15, 1.09 (4s, 18H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ 158.1, 155.6 (7-Flu), 149.5, 149.4, 146.2, 145.6, 142.7, 142.5, 141.7, 141.6, 138.9, 138.5 (Flu), 134.3, 133.3, 132.3, 131.1, 126.6, 126.3, 125.2, 124.9 (FluH), 124.6, 124.1, 124.0, 123.5, 123.4, 119.3, 118.8 (CpH), 58.1, 55.7 (9-Flu), 41.1, 40.8 ($C(CH_3)_2$), 40.6, 39.5 (CpCH_2), 34.7 ($C(CH_3)_3$), 31.2 ($C(CH_3)_3$), 25.4, 23.7 ($C(CH_3)_2$). Elemental analysis calcd (%) for $C_{81}H_{84}$ (1057.53): C 91.99, H 8.01; found: C 91.66, H 7.93;

ESI-MS [$C_{81}H_{84}$] (1056.66) [*m/z*] = 1079.65 ([M + Na]$^+$), 1056.65 ([M]$^+$), 950.85 ([M - Me_2CCp]$^+$), 107.08 ([Me_2CCp]$^+$).

1,3,5-Tris(9-(2-(cyclopenta-1,3-dien-1-yl)propan-2-yl)-9*H*-6,7-(C_8H_{16})-fluoren-2-yl)benzene, Ph{Me_2C(2-(^{Tet}FluH))(CpH)}$_3$ (3d). Using a protocol similar to that described for **3a**, compound **3c** was obtained from **2d** (2.60 g, 2.88 mmol), *n*-BuLi (3.6 mL of a 2.5 M solution in hexane, 9.1 mmol) and 6,6´-dimethylfulvene (0.965 g, 9.1 mmol). **3d** was isolated as a pale yellow solid (2.75 g, 2.12 mmol, 74%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.83 (m, 3H), 7.76 (m, 6H), 7.71 (s, 3H, Ph*H*), 7.68 (m, 3H), 7.57, 7.47 (2m, 3H), 7.21, 7.08 (2m, 3H), 7.04, 6.71, 6.59, 6.52, 6.24, 6.02 (6m, 9H, Cp*H*), 4.25, 4.20 (2s, 3H, Flu*H*), 3.29, 3.11 (2s, 6H, CpH_2), 1.75 (m, 12H, CH_2), 1.43(s, 9H, C(CH_3)$_2$), 1.39 (s, 9H C(CH_3)$_2$), 1.28 (m, 18H, C(CH_3)$_2$), 1.18 (m, 18H C(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 146.2, 143.7, 143.1, 142.8, 139.1, 134.3, 133.5, 132.5, 131.1, 126.6, 126.3, 124.9, 124.4, 119.2, 117.0, 57.9, 55.5 (9-Flu), 51.3 (*C*(CH_3)$_2$), 40.7, 39.6 (Cp*C*H_2), 35.3 (*C*H_2*C*H_2), 34.6, 34.5 (*C*(CH_3)$_2$), 32.2, 31.8 (C(*C*H_3)$_2$), 25.6, 24,7 (C(*C*H_3)$_2$). Elemental analysis calcd (%) for $C_{93}H_{102}$ (1219.80): C 91.57, H 8.43; found: C 91.33, H 8.29; ESI-MS (*m/z*): 1257.763 ([M + K]$^+$).

Ph({Me_2C(2-(6-^{tBu}Flu))(C_5H_4)}$ZrCl_2$)$_3$ (4b-Zr). To a suspension of **3b** (840 mg, 0.80 mmol) in diethyl ether (50 mL) was added *n*-BuLi (2.00 mL of a 2.5 M solution in hexane, 5.00 mmol) at 50 °C under stirring. After 12 h, the reaction mixture was cooled down to room temperature and anhydrous $ZrCl_4$ (583 mg, 2.50 mmol) was added to the sample in the glovebox. The resulting purple/red reaction mixture was stirred at 50 °C for 24 h. Then volatiles were removed *in vacuo* and the remaining solid was suspended in CH_2Cl_2 (50 mL). The suspension was filtered over celite under argon. Removal of the solvent in vacuum yielded the desired complex **4b-Zr** as a pink solid. For additional purification, the crude product was dissolved in benzene (10 mL) followed by precipitation by addition of hexane (15 mL). The clear supernatant solution was decanted and the slurry was washed with hexane (10 mL). After drying *in vacuo*, **4b-Zr** was obtained as a pink powder (1.02 g, 0.66 mmol, 83%). ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ 8.26 (d, *J* = 8.6, 3H), 8.14 (d, *J* = 8.8, 3H), 8.11 (s, 3H), 7.94 (m, 3H), 7.84 (s, 3H, Ph*H*), 7.82 (d, *J* = 8.5, 6H), 7.76 (dd, *J* = 8.9, 1.4, 5H), 6.37 (m, 6H, Cp*H*), 5.87 (q, *J* = 2.8, 3H, Cp*H*), 5.80 (q, *J* = 2.7, 3H, Cp*H*), 2.49, 2.48 (2s, 18H, $C(CH_3)_2$), 1.42 (s, 27H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2, 25 °C): δ 152.3 (6-Flu), 142.9, 141.4, 126.2, 125.3, 125.0, 124.1, 123.3, 122.7, 122.2, 122.0, 121.3, 119.4, 119.0 (FluH), 118.7 (CpH), 114.6 (Cp), 101.9, 101.7 (CpH), 79.5 (9-Flu), 40.6 ($C(CH_3)_2$), 35.4 ($C(CH_3)_3$), 30.7, 28.8 ($C(CH_3)_2$). Elemental analysis calcd (%) for $C_{81}H_{78}Cl_6Zr_3$ (1537.88): C 63.26, H 5.11; found: C 63.55, H 5.32.

Ph({Me$_2$C(2-(7-^{tBu}Flu))(C$_5$H$_4$)}ZrCl$_2$)$_3$ (4c-Zr). Using a protocol similar to that described for **4b-Zr**, complex **4c-Zr** was prepared from **3c** (0.86 g, 0.81 mmol), *n*-BuLi (2.05 mL of a 2.5 M solution in hexane, 5.12 mmol) and $ZrCl_4$ (0.596 g, 2.55 mmol); it was isolated as a pink powder (1.10 g, 0.72 mmol, 88%). ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 8.14 (m, 3H), 8.11 (s, 3H), 7.95-7.86 (m, 9H), 7.68 (s, 3H, Ph*H*), 7.57 (dd, *J* = 8.9, 1.4, 3H), 6.22 and 6.20 (2m, 3H, Cp*H*), 6.13 (m, 3H, Cp*H*), 5.62, 5.59 (2m, 3H, Cp*H*), 5.55 (m, 3H, Cp*H*), 2.09, 2.05 (2s, 9H, $C(CH_3)_2$), 2.01 and 2.00 (2s, 9H, $C(CH_3)_2$), 1.30 (s, 27H $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 25 °C): δ 151.6 (7-Flu), 144.1, 141.9, 126.8, 125.6, 125.3, 124.6, 124.4, 123.2, 122.8, 122.3, 122.0, 121.5, 119.2 (FluH), 118.8, 118.4 (CpH), 114.6 (Cp), 101.6, 101.0 (CpH), 79.4 (9-Flu), 40.2 ($C(CH_3)_2$), 35.1 ($C(CH_3)_3$), 31.9, 30.7, 28.4, 28.2 ($C(CH_3)_2$). Elemental analysis calcd (%) for $C_{81}H_{78}Cl_6Zr_3$ (1537.88): C 63.26, H 5.11; found: C 62.95, H 5.37.

Ph({Me$_2$C(2-(^{Tet}Flu))(C$_5$H$_4$)}ZrCl$_2$)$_3$ (4d-Zr): Using a protocol similar to that described for **4b-Zr**, complex **4d-Zr** was prepared from **3d** (0.96 g, 0.79 mmol), *n*BuLi (1.98 mL of 2.5M solution in hexane, 4.96 mmol) and $ZrCl_4$ (0.578 g, 2.47 mmol); it was isolated as a red powder (1.19 g, 0.64 mmol, 81%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 8.15 (m, 3H), 8.11 (m, 3H), 8.08

(s, 3H), 7.93 (m, 3H), 7.86 (m, 3H), 7.66 (s, 3H, Ph*H*), 6.23 (m, 3H, Cp*H*), 6.11 (m, 3H, Cp*H*), 5.55 (m, 6H, Cp*H*), 2.09, 2.03, 2.00, 1.97 (4s, 18H, $\mathrm{C(C}H_3)_2$), 1.66 ,and 1.62 (2m, 12H, $\mathrm{C}H_2$), 1.36, 1.36, 1.33, 1.27 (4s, 36H, $\mathrm{C(C}H_3)_2$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 147.4, 145.9, 128.3, 127.8, 127.6, 127.0, 125.3, 122.2, 121.9, 120.6 (FluH), 118.9, 118.5 (CpH), 114.0 (Cp), 101.5, 100.6 (CpH), 77.9 (9-Flu), 40.0 ($C\mathrm{(CH_3)_2}$), 35.0 ($C\mathrm{(CH_3)_2}$), 34.8, 34.7, 33.7 ($C\mathrm{H_2}C\mathrm{H_2}$), 32.4, 32.3, 32.1 ($\mathrm{C(}C\mathrm{H_3)_2}$), 28.3, 28.1 ($\mathrm{C(}C\mathrm{H_3)_2}$). Elemental analysis calcd (%) for $\mathrm{C_{93}H_{96}Cl_6Zr_3}$ (1700.15): C 65.70, H 5.69; found: C 66.8, H 6.2.

Ph({Me$_2$C(2-(6-$^{t\mathrm{Bu}}$Flu))(C$_5$H$_4$)}HfCl$_2$)$_3$ (4c-Hf). Using a protocol similar to that described for **4b-Zr**, complex **4c-Hf** was prepared from **3c** (0.86 mg, 0.81 mmol), *n*BuLi (2.05 mL of 2.5M solution in hexane, 5.12 mmol) and $\mathrm{HfCl_4}$ (820 mg, 2.55 mmol); it was isolated as a yellow powder (0.82 g, 0.45 mmol, 56%). ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 8.20 (m, 3H), 8.14 (s, 3H), 7.89 (m, 6H), 7.73 (m, 3H), 7.55 (m, 3H), 7.42 (m, 3H) 6.20, 6.07 (2m, 6H, Cp*H*), 5.53 and 553 (2m, 6H, Cp*H*), 2.10, 2.07, 2.03, 2.02 (4s, 18H, $\mathrm{C(C}H_3)_2$), 1.31 (s, 27H, $\mathrm{C(C}H_3)_3$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 151.4 (6-Flu), 144.1, 141.7, 125.2, 124.3, 124.2, 122.1, 122.0, 121.7, 120.6, 120.0 (FluH), 118.0, 117.8 (Cp), 117.1, 117.1, 99.1, 98.5 (CpH), 79.6 (9-Flu), 40.3 ($C\mathrm{(CH_3)_2}$), 35.0 ($C\mathrm{(CH_3)_3}$), 30.8, 28.7, 28.5 ($\mathrm{C(}C\mathrm{H_3)_2}$). Elemental analysis calcd (%) for $\mathrm{C_{81}H_{78}Cl_6Hf_3}$ (1799.67): C 54.06, H 4.37; found: C 54.81, H 4.95.

Ph({Me$_2$C(2-($^{\mathrm{Tet}}$Flu))(C$_5$H$_4$)}HfCl$_2$)$_3$ (4d-Hf). Using a protocol similar to that described for **4b-Zr**, complex **4d-Hf** was prepared from **3d** (0.86 mg, 0.70 mmol), *n*BuLi (1.77 mL of 2.5M solution in hexane, 4.44 mmol) and $\mathrm{HfCl_4}$ (0.711 g, 2.22 mmol); it was isolated as a yellow powder (0.86 g, 0.44 mmol, 63%). ^{1}H NMR data from 2D HSQC NMR (500/125 MHz, $\mathrm{CD_2Cl_2}$, 25 °C) δ 8.26, 8.15, 7.90 (Flu*H*), 7.84 (Ph*H*), 7.78, 7.75 (Flu*H*), 6.28, 5.79, 5.72 (Cp*H*), 2.47, 2.44 ($\mathrm{C(C}H_3)_2$), 1.81, 1.76 ($\mathrm{C}H_2$), 1.47, 1.42, 1.34, 1.31 ($\mathrm{C(C}H_3)_2$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ (125 MHz, $\mathrm{CD_2Cl_2}$, 25 °C): δ 124.8, 121.7, 124.9 (FluH), 119.9 (PhH), 126.1, 117.4 (Flu), 117.9 (CpH), 116.6 (Cp), 99.0, 98.9 (CpH), 77.6 (9-Flu), 40.7 (*C*(CH$_3$)$_2$), 35.1, 35.1 (*C*H$_2$*C*H$_2$), 32.0 (C(*C*H$_3$)$_2$), 29.0 (C(*C*H$_3$)$_2$). No satisfactory elemental analysis could be obtained for this compound.

Ph({Me$_2$C(2-(7-^{tBu}Flu))(C$_5$H$_4$)}ZrMe$_2$)$_3$ (5c-Zr). To a solution of **4c-Zr** (154 mg, 0.10 mmol) in toluene (15 mL) was added BrMgMe (0.21 mL of a 3.0M solution in diethyl ether, 0.63 mmol) at room temperature under stirring. The resulting solution was stirred at 70 °C overnight. Then volatiles were evaporated *in vacuo* and the residue was extracted with heptane (ca. 15 mL) to give **5b-Zr** as a yellow powder (108 mg, 0.77 mmol, 77%). ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 8.12 (s, 3H), 8.07 (q, *J* = 1.9, 3H), 8.01 (dd, *J* = 8.6, 2.1, 3H), 7.98 (d, *J* = 8.8, 3H), 7.79 (m, 3H), 7.68 (s, 3H, Ph*H*), 7.46 (dd, *J* = 8.8, 1.5, 3H), 6.20 (dq, *J* = 5.4, 2.7, 3H, Cp*H*), 6.14 – 6.11 (m, 3H, Cp*H*), 5.56 (q, *J* = 2.8, 3H, Cp*H*), 5.50 (q, *J* = 2.7, 3H, Cp*H*), 2.04 (s, 9H, C(C*H*$_3$)$_2$), 1.99 (s, 9H, C(C*H*$_3$)$_2$), 1.30 (s, 27H, C(C*H*$_3$)$_2$), –0.92 (s, 9H, Zr-C*H*$_3$), –1.08 (s, 9H, Zr-C*H*$_3$). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 25 °C): δ 149.7 (7-Flu), 140.2, 125.0, 124.6, 124.3, 123.6, 122.0, 121.9, 121.2, 118.6, 118.1, 117.8, 113.0, 112.9 (CpH), 108.9, 101.0, 100.7(CpH), 76.7 (9-Flu), 40.1 (*C*(CH$_3$)$_2$), 35.0 (*C*(CH$_3$)$_3$), 33.2, 32.6 (Zr-*C*H$_3$), 31.0 , 28.8, 28.6 (C(*C*H$_3$)$_2$). Elemental analysis calcd (%) for C$_{87}$H$_{96}$Zr$_3$ (1410.47): C 73.83, H 6.84; found: C 74.01, H 7.11.

Ph({Me$_2$C(2-(^{Tet}Flu))(C$_5$H$_4$)}ZrMe$_2$)$_3$] (5d-Zr). Using a protocol similar to that described for **5c-Zr**, complex **5d-Zr** was prepared from **4d-Zr** (170 mg, 0.10 mmol) and BrMgMe (0.21 mL of a 3.0M solution in diethyl ether, 0.63 mmol); it was isolated as an orange powder (111 mg, 71 µmol, 71%). ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 8.37 (m, 3H), 8.25 (s, 3H), 7.98 (m, 3H), 7.80 (s, 3H, Ph*H*), 7.79 (m, 3H), 7.71 (s, 3H), 6.29 (m, 6H, Cp*H*), 5.65-5.56 (m, 6H, Cp*H*), 2.24 (s, 9H, C(C*H*$_3$)$_2$), 2.22 (s, 9H, C(C*H*$_3$)$_2$), 1.80 (m, 12H, C*H*$_2$), 1.51 (s, 9H, C(C*H*$_3$)$_2$), 1.50 (s, 9H, C(C*H*$_3$)$_2$), 1.45 (s, 9H, C(C*H*$_3$)$_2$), 1.31 (s, 9H, C(C*H*$_3$)$_2$), –1.43 (s, 9H, Zr-C*H*$_3$), –1.51 (s, 9H, Zr-C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, CD$_2$Cl$_2$, 25 °C): δ 145.9 (7-Flu), 145.8 (6-Flu) 143.5, 142.3, 139.7, 139.6 (Flu), 125.9 124.4, 123.2, 121.3(FluH), 121.0 (PhH), 112.8, 112.5 (CpH), 100.8

(CpH), 75.0 (9-Flu), 40.1 ($C(CH_3)_2$), 35.1 (CH_2CH_2), 34.5, 33.5, 32.5, 32.1 ($C(CH_3)_2$), 31.9(Zr-CH_3), 29.7, 28.9 ($C(CH_3)_2$). No satisfactory elemental analysis could be obtained for this compound.

Ph({Me_2C(2-(7-^{tBu}Flu))(C_5H_4)}Zr(CH_2SiMe_3)$_2$)$_3$ (6c-Zr). Using a protocol similar to that described for **5c-Zr**, complex **6c-Zr** was prepared from **4c-Zr** (77 mg, 50 µmol) and $ClMgCH_2SiMe_3$ (0.31 mL of a 1.0M solution in diethyl ether, 0.31 mmol); it was isolated as a yellow powder (81 mg, 44 µmol, 80%). ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 8.40-8.32 (m, 3H), 8.31-8.21 (m, 3H), 8.07-8.02 (m, 3H), 7.99-7.92 (m, 3H), 7.90-7.85 (m, 3H), 7.64 (s, 3H, Ph*H*), 7.46- 7.40 (m, 3H), 6.65-6.43 (m, 6H), 5.84- 5.52 (m, 6H), 2.22, 2.15, 2.10, 2.00 (m, 18H), 1.35, 1.30 (2s, 27H, $C(CH_3)_3$), 0.17-0.09 (m, 27H, $Si(CH_3)_2$), 0.06 (s, 27H, $Si(CH_3)_2$), –0.86-–1.03 (m, 3H, Zr-CH_bH_c), –1.49 (d, J = 11.7, 3H, Zr-CH_aH_b), –1.91 (d, J = 11.7, 3H, Zr-CH_cH_d), –2.05 and –2.08 (2d, J = 11.7, 3H, Zr-CH_aH_b). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C): δ 149.5 (7-Flu), 142.9, 142.8, 139.6, 139.4, 139.3, 126.8, 125.8, 123.2, 122.2, 122.0, 121.5, 118.7 (PhH), 111.7 (Cp) 111.1, 110.3, 101.2, 100.6 (CpH), 77.8 (9-Flu), 50.4, 48.6, 45.2, 44.9 (Zr-CH_2), 35.0 ($C(CH_3)_3$), 31.5, 31.0 ($C(CH_3)_3$), 39.8($C(CH_3)_2$), 28.9, 28.6 ($C(CH_3)_2$), 3.4, 2.8 ($Si(CH_3)_3$). Repeated elemental analyses returned low C content for this compound. calcd (%) for $C_{105}H_{144}Si_6Zr_3$ (1848.45): C 68.23, H 7.85; found: C 65.98, H 7.52.

PGSE Measurements. PGSE NMR experiments were performed on a Bruker Avance DRX 400 spectrometer equipped with a GREAT 1/10 gradient unit and direct QNP probe with a Z-gradient coil, using the following parameters: 298 K, no spinning; spectral width = 4807 Hz; 90° pulse width of 11.5 µs; a diffusion delay time of 0.05 s; a total diffusion-encoding pulse width of 0.0016 s; the diffusion encoding pulse strength from 0 to 35 $G\cdot cm^{-2}$ over 12 or 16 increments with 4 dummy scans and 8 scans per increment. The translational coefficients D_t were determined as previously reported.[20,13]

Polymerization Experiments. Experiments were performed in a 300 mL high pressure glass reactor equipped with a mechanical stirrer (Pelton turbine) and externally heated with a double mantle with a thermostated circulating water bath. The reactor was charged with toluene (150 mL) and MAO (1.5 mL of a 30 wt-% solution in toluene), and propylene (5 bar, Air Liquide, 99.99%) or ethylene (5 bar, Air Liquide, 99.99%) was introduced. The reactor was thermally equilibrated at the desired temperature for 30 min. Monomer gas pressure was decreased to 1 bar, and a solution of the catalyst precursor in toluene (ca. 2 mL) was added by syringe. The monomer gas pressure was immediately increased to 5 bar (kept constant with a back regulator) and the solution was stirred for the desired time. The temperature inside the reactor was monitored using a thermocouple. The polymerization was stopped by venting the vessel and quenching with a 10 wt.% solution of aqueous HCl in methanol (ca. 6 mL). The polymer was precipitated in methanol (ca. 500 mL) and 35 wt% aqueous HCl (ca. 10 mL) was added to dissolve possible catalyst residues. The polymer was collected by filtration, washed with methanol (ca. 200 mL), and dried under vacuum overnight.

Crystal Structure Determination of 2c. Diffraction data were collected at 100 K using a Bruker APEX CCD diffractometer with graphite-monochromatized MoKα radiation (λ = 0.71073 Å). A combination of ω and θ scans was carried out to obtain a unique data set. The crystal structures were solved by direct methods, remaining atoms were located from difference Fourier synthesis followed by full-matrix least-squares refinement based on F2 (programs SIR97 and SHELXL-97).[21] Many hydrogen atoms could be located from the Fourier difference analysis. Other hydrogen atoms were placed at calculated positions and forced to ride on the attached atom. The hydrogen atom positions were calculated but not refined. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystal data and details of data collection and structure refinement for the different compounds are given in Table S1. Crystal data, details of data collection and structure refinement for compound **2c** (CCDC 1863112) can be obtained from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details. All calculations were performed with the TURBOMOLE program package using density functional theory (DFT).[22,23,24,25] The gradient corrected density functional BP86 in combination with the resolution identity approximation (RI)[26,27] was applied for the geometry optimizations of stationary point. A triple-ζ zeta valence quality basis set def-TZVP was used for all atoms.[28] The stationary points were characterized as energy minima (no negative Hessian eigenvalues) by vibrational frequency calculations at the same level of theory.

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Highlights

- Design of an original 1,3,5-phenylene-tris(isopropylidene-bridged cyclopentadienyl/fluorenyl) platform
- Synthesis of trinuclear group 4 tris(*ansa*-metallocene) complexes
- Polymerization catalysis of ethylene and propylene and ethylene/1-hexene