



Cite this: DOI: 10.1039/d6dt00602g

Ph₂Si-bridged constrained-geometry complexes of hafnium and titanium for copolymerization of ethylene and 1-octene: an experimental and computational comparison

Ekaterina Kuchuk,^a Kaitie A. Giffin,^c Alexandre Welle,^c Katty Den Dauw,^c Alvaro Fernandez,^c Marie Cordier,^b Thierry Roisnel,^b Jean-Francois Carpentier^{id}*^a and Evgueni Kirillov^{id}*^a

A series of new constrained-geometry hafnium and titanium complexes, including {Me₂Si(2,7-tBu₂Flu)NtBu}HfCl₂ (**1-HfCl₂**), {Ph₂Si(2,7-tBu₂Flu)NtBu}HfCl₂ (**2-HfCl₂**) and {Ph₂Si(2,7-tBu₂Flu)NtBu}TiCl₂ (**2-TiCl₂**), was synthesized and fully characterized using solution NMR spectroscopy and X-ray crystallography. These complexes were subsequently evaluated in the copolymerization of ethylene with 1-octene ([C₈]₀ = 0.48–1.88 M), revealing striking differences in catalytic performance and properties of the resulting polyolefin elastomers/plastomers (POE/POP). The hafnium complexes **1-HfCl₂** and **2-HfCl₂** exhibited low catalytic activity, yielding polymers with broad molecular weight distributions and only modest incorporation of 1-octene. In contrast, the titanium complex **2-TiCl₂** demonstrated significantly higher catalytic activity and achieved substantial 1-octene incorporation at an ethylene/1-octene molar ratio of ca. 6 : 1, with values reaching up to 36.6 mol%. **2-TiCl₂** exhibited approximately half the productivity of benchmark CGC {Me₄CpSiMe₂NtBu}TiCl₂ (**3-TiCl₂**), yet yielding POE with a much higher molecular weight and a density of 0.8547 g cm⁻³. DFT calculations were also performed for the cationic catalytic species derived from the pre-catalysts **2-HfCl₂** and **2-TiCl₂** to rationalize the relative performance of the titled systems in incorporating ethylene and 1-octene and undergoing termination and transfer reactions. A +5.6 kcal mol⁻¹ energy difference (in terms of ΔΔH[‡]) was computed between the transition states for the third ethylene insertion into the M–C(polymeryl) bond for the Hf-based system compared to the Ti-based system; other phenomena possibly plaguing efficiency of the Hf-system are discussed.

Received 11th March 2026,
Accepted 21st April 2026

DOI: 10.1039/d6dt00602g

rsc.li/dalton

Introduction

Group 4 metal constrained-geometry catalysts (CGC)^{1,2} remain one of the most extensively studied families of catalysts, known for their remarkable efficiency in producing ethylene/ α -olefin (e.g. 1-octene) copolymers. These copolymers are of high industrial relevance for applications in coatings, car tires, polymer blends, foams, and impact modifiers used in polypropylene for automotive components.³ The versatility and efficiency of CGC systems, essentially those based on Ti and Hf, have made them indispensable in the production of such advanced materials with tailored properties. The molecular

masses and comonomer incorporation levels of ethylene/1-octene copolymers synthesized with CGC systems are highly dependent on the structure of the (pre)catalyst. By modulating the ligand environment, CGC systems enable precise control over polymer properties, such as elasticity, toughness, low-temperature ductility, making them an essential tool in polymer chemistry. A landmark achievement in CGC technology is its successful commercialization by Dow through the INSITE™ technology, which revolutionized the production of specialty polyolefins. In line with its industrial success, academic interest in CGC systems persists due to the extensive structural diversity of potential catalyst designs and the opportunities for further optimization.⁴

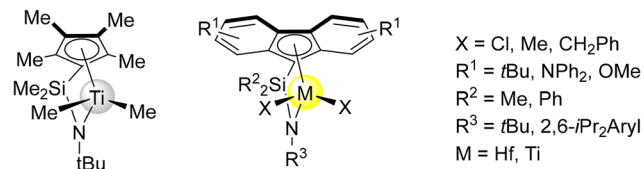
The original CGC Ti system featuring a {Me₄CpSiMe₂NtBu} ligand unit (Scheme 1, left)⁵ demonstrates exceptionally high productivity in the copolymerization of ethylene and 1-octene, producing materials with high comonomer incorporation.^{6,7} However, the resulting copolymers often exhibit relatively low molecular weights, which can limit their applicability in some

^aUniv Rennes, CNRS, Institut des Sciences Chimiques de Rennes (ISCR), UMR 6226, F-35042 Rennes, France. E-mail: jean-francois.carpentier@univ-rennes.fr, evgueni.kirillov@univ-rennes.fr

^bCentre de diffraction X, Univ Rennes, CNRS, ISCR, UMR 6226, F-35700 Rennes, France

^cTotalEnergies OneTech Belgium, Zone Industrielle Feluy C, B-7181 Seneffe, Belgium





Scheme 1 Prototypical CGC titanium (left) and related (fluorenyl-amido) group 4 metal (right) (pre)catalysts.

contexts. Ongoing research has sought to address such challenges, exploring novel ligand frameworks and metal centers to enhance the performance of group 4 metal CGC systems.

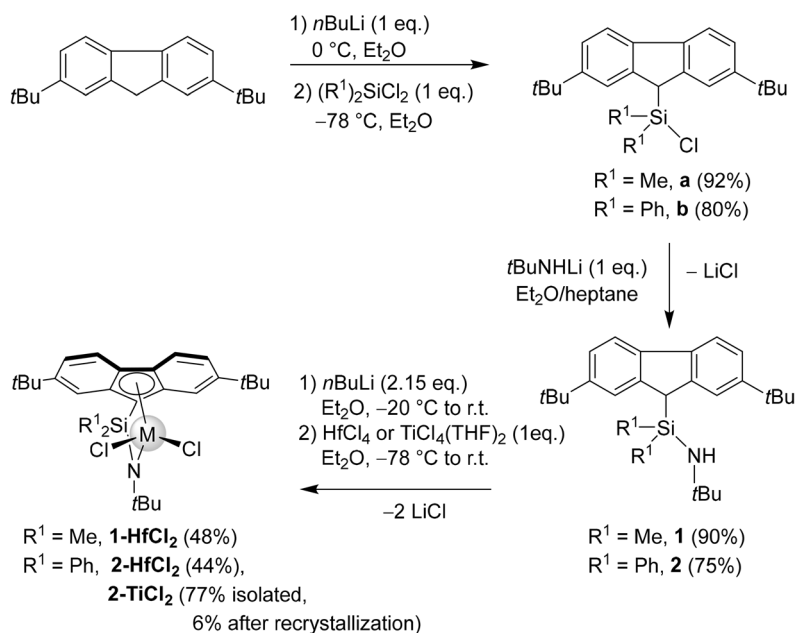
Thus, the modification of CGC systems through the introduction of bulky substituted fluorenyl moieties (e.g., 2,7-*t*Bu₂-Flu, 3,6-*t*Bu₂-Flu, Oct = octamethyloctahydrofluorene)^{8–26} or other structural modifications²⁷ in place of the Me₄Cp moiety, as well as varying substituents on the nitrogen atom, remains a widely explored strategy for fine-tuning the geometry and electronic properties, and in turn the catalyst's performance of CGC systems. As part of studies aimed at varying the nature of the metal center, fluorenyl-zirconium-based CGC systems have also been extensively investigated over the past decades, highlighting the specific role of steric expansion of the fluorenyl moiety in stabilizing the catalyst in its active form.^{28–32}

In recent years, entirely new types of geometrically constrained titanium complexes have been synthesized, broadening the scope of CGC designs.³³ Numerous research groups have investigated these systems in various polymerization processes, essentially focusing on the homo- and co-polymerization of ethylene, e.g. ethylene/propylene, ethylene/1-octene, ethylene/norbornene,^{8–10,13,16–19,23–26,34,35} but also polymerization of methyl methacrylate (MMA), 1,3-butadiene and styrene.^{15,20,27,36,37}

In the present study, we investigated the catalytic potential of a series of new fluorenyl-based CGC complexes incorporating either Me₂Si- or the bulkier Ph₂Si-bridge (Scheme 1, right) for the copolymerization of ethylene with 1-octene. Given the distinct advantages of hafnium-based polymerization catalysts, which may exhibit greater thermal stability than their titanium (and zirconium) counterparts,^{38,39} – a feature essential for high-temperature solution polymerization processes –, our approach was to synthesize and evaluate complexes of both metals. The dual focus on Ti and Hf CGC complexes aims at leveraging the individual strengths of these metals, with Ti systems potentially offering enhanced incorporation efficiency and Hf systems possibly providing a better thermal stability under demanding (co)polymerization conditions.

Results and discussion

The synthesis of the fluorenyl-amine proligands **1** and **2** was achieved by a regular two-step approach (Scheme 2).⁴⁰ The consistency of the products was confirmed by ¹H NMR spectroscopy (see the SI, Fig. S1 and S2 for **1** and **2**, respectively). The proligands were then used for the synthesis of the corresponding hafnium (**1-HfCl₂**, **2-HfCl₂**) and titanium (**2-TiCl₂**) complexes, following a regular salt-metathesis approach. Hafnium complexes were isolated in 48% and 44% yields, respectively, as light-yellow powders. **2-TiCl₂** was recovered after workup as a dark-violet solid in 77% yield, which after recrystallization afforded crystals in 6% yield. The consistency and purity of these complexes were confirmed by ¹H and ¹³C NMR spectroscopy (Fig. S3–S8, respectively), X-ray crystallographic studies and combustion analysis.



Scheme 2 Synthesis of proligands **1** and **2** and corresponding CGC complexes **1-HfCl₂**, **2-HfCl₂** and **2-TiCl₂**.



Table 1 Selected bond distances (Å) and angles (°) for CGC complexes **1-HfCl₂**, **2-HfCl₂·(C₆H₆)** and **2-TiCl₂·(C₆H₆)** and reference complexes **I-Hf** and **II-Ti**

	I-Hf ²⁸	1-HfCl₂	2-HfCl₂·(C₆H₆)	II-Ti ²³	2-TiCl₂·(C₆H₆)
M–Cl(1)	—	2.3645(8)	2.3656(6)	—	2.2688(5)
M–Cl(2)	—	2.3696(8)	2.3691(6)	—	2.2649(4)
M–N	2.087(8)	2.015(2)	2.0300(17)	1.922(12)	1.9093(12)
M–C(1)	2.373(11)	2.351(3)	2.343(2)	2.250(14)	2.210(14)
M–C(2)	2.550(10)	2.474(3)	2.516(2)	2.384(14)	2.433(14)
M–C(3)	2.685(11)	2.610(3)	2.619(2)	2.599(14)	2.595(15)
M–C(4)	2.697(13)	2.613(3)	2.587(2)	2.615(15)	2.558(14)
M–C(5)	2.500(13)	2.479(3)	2.426(2)	2.430(15)	2.334(14)
M–Flu _{cent}	2.251(10)	2.185(3)	2.177(2)	2.132(14)	2.098(14)
Flu _{cent} –M–N	105.87(5)	106.38(3)	105.16(2)	111.58(6)	110.52(6)
Cl(1)–M–Cl(2)	—	103.27(3)	103.89(2)	—	102.604(18)
N1–Si–C(1)	97.8(5)	93.97(11)	93.92(9)	94.20(6)	92.01(6)

The solid-state molecular structures of hafnium complexes **1-HfCl₂** and **2-HfCl₂** and titanium complex **2-TiCl₂** are shown in Fig. S9, S10 and 1, respectively. Selected bond distances (Å) and angles (deg) are reported in Table 1. All the geometrical parameters, including bond lengths and angles, and overall coordination environment are comparable with those observed in analogous complexes, e.g. {Me₂Si(Oct)NtBu}Hf(CH₂Ph)₂ (**I-Hf**)²⁸ and {Me₂Si(2,7-*t*Bu₂Flu)N(CMe₂Ph)}TiMe₂ (**II-Ti**)²³ respectively.

Polymerization studies

Copolymerization of ethylene and 1-octene was explored using the hafnium (**1-HfCl₂**, **2-HfCl₂**) and titanium (**2-TiCl₂**) complexes in combination with Al*i*Bu₃ (TIBAL)/[PhNMe₂H]⁺[B(C₆F₅)₄][−] as activator (cocatalyst). Although metallocene/borate cocatalyst systems are typically used with a 1 : 1 stoichiometric ratio, catalyst productivity in such dichlorometallocene/TIBAL/borate systems is known to increase with increasing borate concentration, up to a [B]/[M] molar ratio of 3 : 1.^{41,42} Therefore, this ratio was systematically employed in this study. Representative results obtained from experiments carried out at 35 bar ethylene pressure in a 100 mL reactor magnetically

stirred are reported in Table 2. The productivity observed for **1-HfCl₂** in homopolymerization of ethylene was low (entry 1; 135 kg_{PE} mol_{Hf}^{−1} h^{−1}), in contrast to **2-TiCl₂**, which afforded polyethylene (PE) with a productivity of 3090 kg_{PE} mol_{Ti}^{−1} h^{−1} under similar conditions (entry 6).

In the copolymerization experiments ([C₈]₀ = 0.48–1.88 M), the productivities observed for the hafnium complexes **1-HfCl₂** and **2-HfCl₂** were also quite low (131–141 kg_{Pol} mol_{Hf}^{−1} h^{−1}), regardless of the temperature employed (up to 130 °C) or the nature of the silylene bridge substituents (Me₂Si vs. Ph₂Si) (entries 2–5).[†] In striking contrast, the Ti analogue **2-TiCl₂** exhibited remarkably high productivities at 130 °C (8030–23 780 kg_{Pol} mol_{Ti}^{−1} h^{−1}) over a range of catalyst concentrations ([Ti]₀ = 2.6–11.2 μM; entries 7–10). In general, the productivity of this system in ethylene/1-octene copolymerization was higher than in ethylene homopolymerization, confirming that the so-called “comonomer effect” is operative for **2-TiCl₂**.⁴³

Unexpectedly, the molecular weights (*M_w*) of the copolymers obtained with the Ti-based CGC system were significantly higher than those of the polymers obtained with the Hf ones (compare entries 3 and 7–10, respectively). In these cases, the broad polydispersities observed (*M_w*/*M_n* = *D_M* in the range 3.8–22.2) could indicate apparent multi-site behavior of the catalytic systems under the polymerization conditions employed, with possible contributions from mass-transfer limitations arising from magnetic stirring in the 100 mL reactor (*vide infra*). In the case of systems based on the larger ionic radius Hf, the apparent multi-site behavior may additionally originate from catalyst decomposition on the timescale of a single chain-growth event, as well as from the formation of

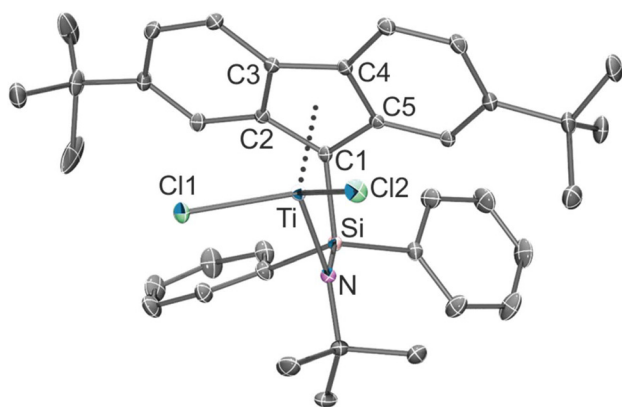


Fig. 1 ORTEP representation of the solid-state molecular structure of **2-TiCl₂·(C₆H₆)** (H atoms omitted for clarity; ellipsoids drawn at the 50% probability level).

[†]The low productivity of the Hf systems may stem from instability or formation of Hf–Al bimetallic adducts (*vide infra*). Deleterious, excessive coordination of PhNMe₂ (released from the activator) to the active cationic hafnium species is likely to be discarded. Indeed, PhNMe₂ is usually considered as a poor base, very weakly or essentially non-coordinating to early transition metals. In fact, reports about the use of pyridylamido hafnium complexes for 1-hexene polymerization and ethylene/1-octene copolymerization (in the presence of Al(*n*-oct)₃; hence quite related to the present investigations) mention essentially identical productivity and polymer characteristics (in 1-hexene homopolymerization) upon activation with either [PhNMe₂H]⁺[B(C₆F₅)₄][−] or [Ph₃C]⁺[B(C₆F₅)₄][−] (see ref. 35).



Table 2 (Co)polymerization of ethylene and 1-octene (C8) with CGC systems 1-HfCl₂, 2-HfCl₂ and 2-TiCl₂^a

Entry	Precat.	[M] ₀ [μM]	Co-cat. [B/M]	Temp. [°C]	[C8] ₀ [M]	m _{Pol} [g]	Productivity [kg _{Pol} mol _{cat} ⁻¹ h ⁻¹]	T _g ^b [°C]	T _c ^b [°C]	T _m ^b [°C]	M _w ^c [×10 ³] [g mol ⁻¹]	M _w / M _n ^c	C ₈ incorp. ^d [mol%]
1	1-HfCl ₂	12.1	3.0	130	0	0.042	135	n.a.	119.8	137.3	n.a.	n.a.	0
2		12.0	3.0	100	1.83	0.044	141	n.o.	111.5	124.4	n.a.	n.a.	n.a.
3		12.0	3.0	130	1.83	0.041	131	n.a.	n.a.	n.a.	78.2	22.2	7.8
4	2-HfCl ₂	11.6	3.1	60	1.83	0.031	103	-59.4	121.8	128.4/123.2/112.9	n.a.	n.a.	n.a.
5		11.4	3.2	100	1.83	0.033	112	-68.4	117.6/112.8	120.4/112.7	n.a.	n.a.	n.a.
6 ^e	2-TiCl ₂	5.8	3.4	130	0	0.45	3 090	n.a.	128.1	134.2	n.a.	n.a.	0
7 ^f		2.6	3.1	130	1.88	1.56	23 780	-66.7	95.8	115.8	496.1	3.8	36.6
8 ^g		5.6	3.4	130	1.84	2.21	15 160	-65.1	67.4/97.6	113.2	366.0	5.7	29.1
9		11.2	3.1	130	1.83	2.97	10 190	-67.3	100.0	114.5	305.4	4.3	29.6
10		11.2	3.2	130	1.83	2.34	8 030	-63.8	73.4/100.9	114.7	629.7	10.7	23.1

^a General polymerization conditions unless otherwise stated: 100 mL-high pressure metallic reactor; solvent: isopar-G; ca. 50 mL of the liquid phase; 35 bar of ethylene; 15 mL (95.6 mmol) of 1-octene (1.83 M, 30% v/v); TIBAL = 0.30 mL neat (*i.e.*, 1.20 mmol, [Al] = 24.0 mM); cocatalyst: [PhNMe₂H]⁺[B(C₆F₅)₄]⁻; reaction time = 30 min; n.a. = not analyzed, n.o. = not observed. ^b Determined by DSC from second run. ^c Determined by SEC in 1,2,4-trichlorobenzene at 135 °C vs. polystyrene standards (uncorrected values). ^d Determined by SEC equipped with a FTIR detector; ^e TIBAL = 0.71 mL of a 1 M solution in toluene (*i.e.*, 0.71 mmol, [Al] = 14.2 mM). ^f TIBAL = 0.32 mL of a 1 M solution in toluene (0.32 mmol, [Al] = 6.4 mM). ^g TIBAL = 0.18 mL neat (0.71 mmol, [Al] = 14.2 mM).

bimetallic species with R₃Al (where R = H, Me, *i*Bu or polymeryl), which may undergo disproportionation or evolve into other complex structures.^{44,45}

The thermal transitions (melting, T_m, crystallization, T_c, and glass transition, T_g) determined for the copolymers obtained with 2-TiCl₂ were found within a narrow range of 2–3 °C, regardless the significant differences in the corresponding molecular weight (M_w = 366.0 and 629.7 kg mol⁻¹) and incorporated 1-octene content (29.1 and 23.1 mol% at [C8]₀ = 1.83 M, respectively; compare entries 8 and 10). The observation of two crystallization transitions (T_c) for both samples may also be attributed to the multi-site nature of these polymerization reactions, which results in different crystallizable polymer fractions.

Two polymerization experiments conducted in a 1 L reactor equipped with mechanical stirring at 100 °C and 32 bar ethylene pressure, and at an ethylene/1-octene molar ratio of ca. 6 : 1 in the presence of H₂, showed similar trends in terms of overall productivity (Table 3). Under these conditions, 1-HfCl₂ proved completely inactive, whereas 2-TiCl₂ exhibited very high productivity (129 730 kg_{Pol} mol_{Ti}⁻¹ h⁻¹). Improved control over the polymerization was achieved, as evidenced by a much narrower polydispersity (D_M = 2.3),[‡] still affording a high molecular weight (M_w = 340.5 kg mol⁻¹). The incorporated 1-octene content (20.1 mol% at [C8]₀ = 0.48 M) highlights the high propensity of this Ti CGC system to incorporate α-olefins (Fig. S15). The corresponding polymer density (0.8547 g cm⁻³) is significantly lower than that of conventional PE (0.91–0.93 g cm⁻³) and falls in the lower limit of the range for typical POP/POE materials (0.86–0.90 g cm⁻³).⁴⁶

[‡] The much narrower dispersity observed in this reactor equipped with efficient mechanical stirring may suggest that the aforementioned large polydispersities observed in the magnetically stirred reactor may actually be arising, at least in part, from mass transfer limitations; yet, a positive effect of H₂ addition as a regenerating and transfer agent is also clearly anticipated under these conditions.

For a direct comparison, the performance of the benchmark CGC {(Me₄Cp)SiMe₂NtBu}TiCl₂ (3-TiCl₂) was evaluated under identical conditions (Table 3, entry 3). The reference catalyst appeared to be nearly twice as productive as 2-TiCl₂, although it afforded a significantly (about one order of magnitude) lower molecular weight copolymer (M_w = 40.1 kg mol⁻¹) and a higher density (0.8601 g cm⁻³).

¹³C NMR analysis of both polymer samples produced by 2-TiCl₂ and 3-TiCl₂ (Table 3, entries 2 and 3) featured similar end-chains, with 29 and 27 saturated end-chains per 10 000 C, respectively, and no vinyl end-groups detected; this hints at very low β-H elimination (*vide infra*).

Theoretical calculations

In order to better rationalize the observed catalytic performance of the Hf- and Ti-based CGC systems, we conducted theoretical (DFT) computations using our previously developed theoretical model.^{47,48}

The Hf and Ti CGC systems showed markedly different computed reactivity trends toward ethylene, within the intrinsic precision limits of the DFT method (Schemes S1, S3 and S4). For example, the first ethylene coordination/insertion into the cationic species [{Ph₂Si(2,7-*t*Bu₂Flu)NtBu}M-Me]⁺ (A, M = Hf or Ti), corresponding to the activation step (Scheme S1), displayed nearly identical reaction enthalpies (Δ_rH = 19.7–20.0 kcal mol⁻¹) for both metals affording [{Ph₂Si(2,7-*t*Bu₂Flu)NtBu}M-*n*-propyl]⁺ (C). However, the process was kinetically more favorable for Ti by ΔΔH[‡] of 6.5 kcal mol⁻¹.

Because the second and third ethylene insertion steps are representative of the overall catalytic performance, they were computed for the cationic complex [{Ph₂Si(2,7-*t*Bu₂Flu)NtBu}M-*n*-propyl]⁺ (C, where M = Hf or Ti). The insertion of 1-octene at the third step, following ethylene insertion, was also evaluated. The main results are summarized in Table 4 and illustrated in Schemes 3 and 4.

The 5.6 kcal mol⁻¹ energy difference (in terms of ΔΔH[‡]) between the transition states (TS) for the third ethylene inser-



Table 3 Copolymerization of ethylene and 1-octene (C8) with CGC systems **1-Hf-Cl₂** and **2-Ti-Cl₂** in the presence of H₂^a

Entry	Precat.	[M] ₀ [μmol]	[B]/ [M]	[C8] ₀ [M]	m _{Pol} [g]	Productivity [kg _{Pol} mol _{cat} ⁻¹ h ⁻¹]	T _g ^b [°C]	T _c ^b [°C]	T _m ^b [°C]	M _w [×10 ³] ^b [g mol ⁻¹]	M _w / M _n ^b	Density ^c [g cm ⁻³]	C8 incorp. ^d [wt%]	C8 incorp. ^d [mol%]
1	1-HfCl₂	0.74	3.0	0.48	0	0	n.a.	n.a.	n.a.	—	—	—	—	—
2	2-TiCl₂	0.74	3.0	0.48	16.0	129 730	-55.1	n.o.	n.o.	340.5	2.3	0.8547	50.3	20.1
3	3-TiCl₂	0.76	3.0	0.48	36.2	285 650	-52.6	n.o.	n.o.	40.1	2.4	0.8601	48.5	19.1

^a General polymerization conditions otherwise stated: 1 L reactor; cocatalyst: [PhNMe₂H]⁺[B(C₆F₅)₄]⁻; solvent: *n*-hexane (425 mL); reaction time = 10 min; 2.0 mL TIBAL (10% v/v in hexane); P_{C₂H₄} = 32 bar; T_{Pol} = 100 °C; H₂ = 800 ppm; n.a. = not analyzed, n.o. = not observed. ^b Determined by SEC in 1,2,4-trichlorobenzene at 135 °C vs. polystyrene standards (uncorrected values). ^c Measured according to the ISO 1183-1:2012 standard method, method A at 23 °C. ^d Determined by ¹³C NMR spectroscopy at 130 °C in C₆D₆/1,2,4-trichlorobenzene.

Table 4 Energetic data (kcal mol⁻¹) calculated for ethylene coordination/insertion, β-H elimination (BHE) and β-H transfer (BHT) steps and TIBAL/TMA coordination with Hf and Ti CGC systems [(Ph₂Si(2,7-*t*Bu₂-Flu)NtBu)M-R]⁺

		CGC system	
		Hf	Ti
2nd insertion	ΔH _{coord}	-2.9	-3.4
	ΔH [‡]	7.8	5.3
	Δ _r H	-20.1	-25.5
3d insertion (ethylene)	ΔH _{coord}	-6.6	-2.9
	ΔH [‡]	8.1	2.5
	Δ _r H	-19.4	-20.7
3d insertion (1-octene after ethylene)	ΔH _{coord}	-7.0	-5.0
	ΔH [‡]	11.2	10.9
	Δ _r H	-12.3	-14.1
BHE	ΔH [‡]	13.7	12.4
	Δ _r H	7.3	12.2
BHT (ethylene)	ΔH [‡]	17.1	11.4
	Δ _r H	-4.4	-3.8
BHT (1-octene)	ΔH [‡]	16.7	20.9
	Δ _r H	-1.2	-3.3
Transfer to H ₂ (after ethylene insertion)	ΔH [‡]	11.8	4.3
	Δ _r H	-13.5	-11.7
Transfer to H ₂ (after 1-octene insertion)	ΔH [‡]	12.3	7.8
	Δ _r H	-13.5	-8.6
Coordination of TIBAL (after ethylene insertion)	Δ _r H	0.9	5.8
Coordination of TMA (after ethylene insertion)	Δ _r H	-6.0	-2.5

tion into the M-C(polymeryl) bond suggests approximately a 10⁴-fold higher polymerization rate for the Ti-based system compared to the Hf-based system (assuming equal comonomer concentrations) at 298 K. This computed difference is in line with the significant differences observed in the productivities of the Hf- and Ti-based systems, emphasizing the very low (co) polymerization efficiency observed with the Hf-based catalysts based on **1,2-HfCl₂**. The insertion of 1-octene following

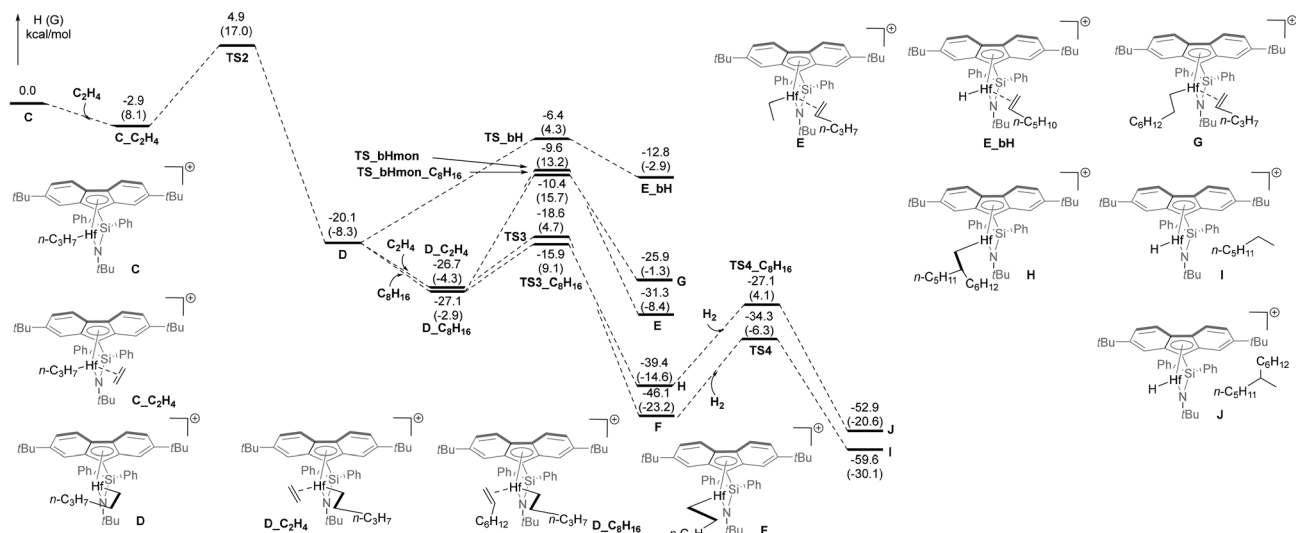
ethylene was found to be only slightly more favorable on thermodynamic grounds (ΔΔ_rH = 1.8 kcal mol⁻¹) in the case of **2-TiCl₂**, while virtually no difference was observed from a kinetic standpoint (ΔΔH[‡] = 0.3 kcal mol⁻¹).

The ability to induce chain-termination reactions was also evaluated (Table 4 and Schemes 3 and 4). Yet, both Hf and Ti CGC systems revealed comparable reluctance toward β-H elimination (BHE) and β-H transfer (BHT) to the monomer (both ethylene and 1-octene) from a kinetic perspective, as indicated by the relatively high barriers compared to those for regular ethylene or 1-octene insertion (ΔH[‡] = 12.4–13.7 and 11.4–20.9 vs. 2.5–7.8 or 10.9–11.2 kcal mol⁻¹, respectively).

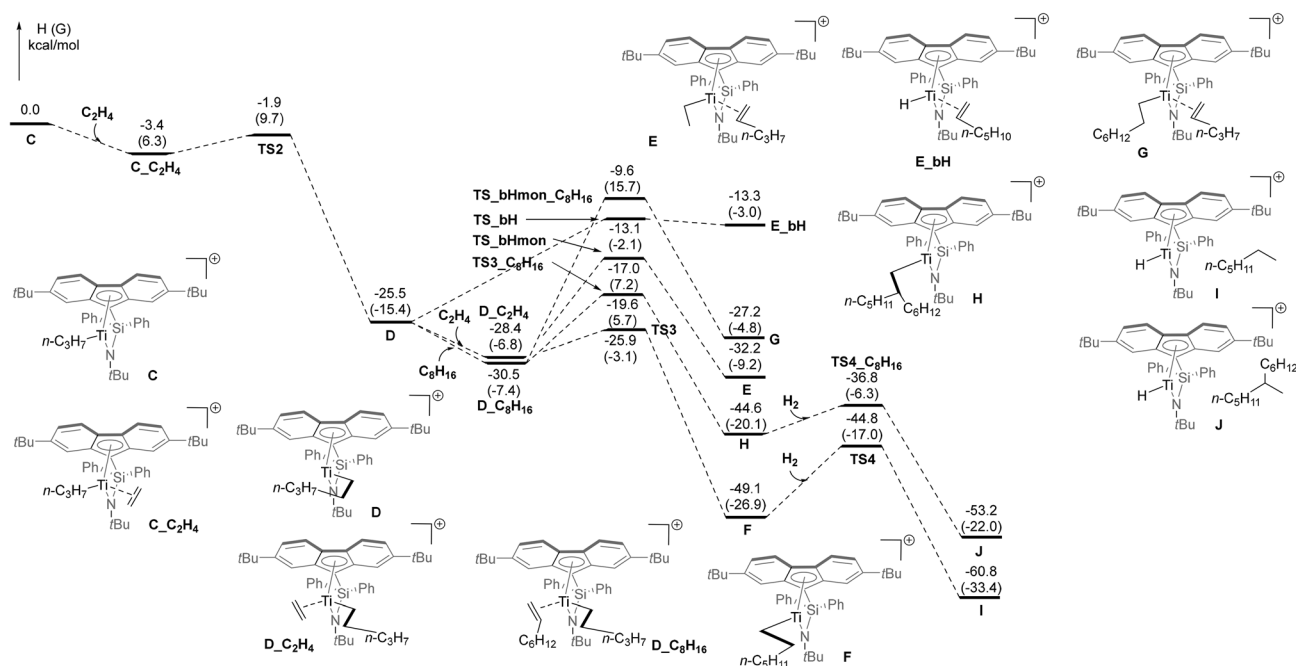
Since small amounts of dihydrogen were introduced in several polymerization experiments (Table 3) to control the molecular weight of the copolymers, transfer-to-hydrogen was also evaluated computationally (Scheme S2). Transfer-to-hydrogen appeared to be kinetically more favorable (ΔΔH[‡] = 2.9–7.5 kcal mol⁻¹) for **2-TiCl₂**, regardless of the nature of the monomer inserted in the previous step. For the **3-TiCl₂** reference system, which produces lower molecular weight copolymers in the presence of hydrogen, the experimental data are consistent with the very low computed barriers (ΔH[‡] = 0.1–0.2 kcal mol⁻¹) and the favorable thermodynamics of this process (Δ_rH = -13.6–16.2 kcal mol⁻¹).

Heterobimetallic ion pairs of the type [(LX)₂M(μ-R)AlR₂]⁺[A]⁻ (where {LX}₂M represents a group 4 metallocene-type core, R is an alkyl group, and [A]⁻ denotes a counteranion such as [“MeMAO”]⁻, [B(C₆F₅)₄]⁻, etc.) are widely recognized as “dormant” species and precursors for chain transfer during olefin polymerization.^{49,50} These species play a pivotal role in polymerization mechanisms, serving as intermediates that maintain the delicate balance between active and dormant states of the catalytic cycle.^{51–54} Hence, we also computationally evaluated the thermochemistry associated with the formation of such heterobimetallic adducts derived from the insertion products, specifically the naked cations [(Ph₂Si(2,7-*t*Bu₂Flu)NtBu)M-*n*-pentyl]⁺ (Scheme 5), with Al*i*Bu₃ (TIBAL, in its dimeric form Al₂*i*Bu₆),⁵⁵ employed in our study as co-activator and scavenger and, for comparison purposes, with AlMe₃ (TMA, in its dimeric form Al₂Me₆)⁵⁶ although it is not directly relevant to our catalysis. Consistent with previous reports on the strong binding affinity of cationic hafnocenes toward

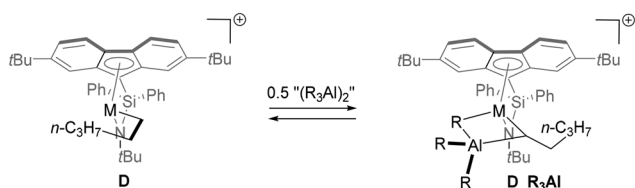




Scheme 3 Energy profile computed for ethylene/1-octene coordination/insertion, β -H elimination (BHE) and β -H transfer (BHT) steps for $\{(\text{Ph}_2\text{Si}(2,7\text{-tBu}_2\text{Flu})\text{NtBu})\text{Hf-}n\text{-propyl}\}^+$ (C) (energies in kcal mol⁻¹ relative to C).



Scheme 4 Energy profile computed for ethylene/1-octene coordination/insertion, β -H elimination (BHE) and β -H transfer (BHT) steps for $\{(\text{Ph}_2\text{Si}(2,7\text{-tBu}_2\text{Flu})\text{NtBu})\text{Ti-}n\text{-propyl}\}^+$ (C) (energies in kcal mol⁻¹ relative to C).



Scheme 5 Reversible formation of heterobimetallic cationic R_3Al -adducts from $\{(\text{Ph}_2\text{Si}(2,7\text{-tBu}_2\text{Flu})\text{NtBu})\text{M-}n\text{-pentyl}\}^+$ (where M = Hf, Ti) and R_3Al dimer (e.g. $\text{Al}_2\text{iBu}_6\equiv\text{TIBAL}$ dimer).

TMA,⁵⁷ our calculations (Table 4) also indicate a higher propensity of the Hf CGC system to reversibly coordinate TIBAL compared to its Ti analogue (and, expectedly, much more TMA than TIBAL). The coordination of TIBAL to the putative cationic alkyl active catalyst species does not appear to be favored; however, the low computed value ($\Delta H_{\text{coord}} = +0.9$ kcal mol⁻¹) for the Hf system suggests that it could represent a competitive deactivation pathway. This phenomenon, which results in blocking of the active site and prevents the coordi-



nation and insertion of olefin molecules, may also contribute to the significantly lower activity observed in the present Hf CGC systems. However, NMR investigations of mixtures of 1-**Hf-Cl₂**/[PhNMe₂H]⁺[B(C₆F₅)₄]⁻/TIBAL yielded highly complex spectra that proved uninformative.

Conclusions

Constrained-geometry dichloro complexes of hafnium and titanium from the {Flu/N}-family were synthesized and evaluated in the copolymerization of ethylene and 1-octene. These preliminary studies revealed that the Hf CGC complexes exhibit very low productivity; this may be attributed essentially to a more difficult insertion of the monomer (ethylene) into the Hf-C(polymeryl) bond as well as to the existence of concomitant deactivation pathways of the active cationic species involving alkylaluminum compounds. On the contrary, the Ti analogue 2-**TiCl₂** exhibited significantly higher productivity in ethylene/1-octene copolymerization, featuring a clear “comonomer effect”. The copolymers obtained with the Ti CGC system also displayed higher molecular weights; narrow polydispersity consistent with single site behavior of this Ti CGC system could be achieved in the presence of H₂ as reactivating/transfer agent in a mechanically stirred reactor. Thermal analysis revealed narrow ranges of melting, crystallization, and glass transition temperatures, with several crystallizable polymer fractions. Furthermore, the present Ti CGC system showed a high propensity to incorporate α -olefins, producing POE/POP-type materials with lower density. The cost-effectiveness of titanium compared to hafnium further enhances the appeal of 2-**TiCl₂** as a promising candidate for large-scale production of POE/POP-type copolymers.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

The authors declare no competing financial interest.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: Fig. S1–S15, Schemes S1 and S2, Tables S1 and S2. See DOI: <https://doi.org/10.1039/d6dt00602g>.

CCDC 2497781–2497783 (1-**HfCl₂**, 2-**HfCl₂** and 2-**TiCl₂**) contain the supplementary crystallographic data for this paper.^{58a–c}

Acknowledgements

This work was financially supported by TotalEnergies OneTech Belgium (postdoctoral fellowship to EAK). The authors are grateful to Jerome Ollivier for technical assistance in DSC analysis. EK gratefully acknowledges the Institut Universitaire de France (IUF) for a Senior IUF fellowship, and thanks ENSCR and the CTI group of ISCR for computational facilities.

References

- 1 A. L. McKnight and R. M. Waymouth, Group 4 *ansa* cyclopentadienyl-amido catalysts for olefin polymerization, *Chem. Rev.*, 1998, **98**, 2587–2598.
- 2 H. Braunschweig and F. M. Breitling, Constrained Geometry Complexes – Synthesis and Applications, *Coord. Chem. Rev.*, 2006, **250**, 2691–2720.
- 3 F. Li and W. Liu, Progress in the catalyst for ethylene/ α -olefin copolymerization at high temperature, *Can. J. Chem. Eng.*, 2023, **101**, 4992–5019.
- 4 P. S. Chum and K. W. Swogger, Olefin polymer technologies - History and recent progress at The Dow Chemical Company, *Prog. Polym. Sci.*, 2008, **33**, 797–819.
- 5 J. Okuda, Functionalized Cyclopentadienyl Ligands, IV. Synthesis and Complexation of Linked Cyclopentadienyl-Amido Ligands, *Chem. Ber.*, 1990, **123**, 1649–1651.
- 6 J. Klosin, P. P. Fontaine and R. Figueroa, Development of Group IV molecular catalysts for high temperature ethylene- α -olefin copolymerization reactions, *Acc. Chem. Res.*, 2015, **48**, 2004–2016.
- 7 S.; Bremer, R. J. Bellair, T. W. Scholtz, T. D. Senecal and J. Klosin, Synthesis and evaluation of trialkyl ammonium tetrakis(pentafluorophenyl) aluminate, a highly efficient activator for high-temperature ethylene- α -olefin copolymerization reactions, *Organometallics*, 2024, **43**, 2651–2661.
- 8 A. Razavi and U. Thewalt, Preparation and crystal structures of the complexes (η^5 -C₅H₃ TMSCMe₂ η^5 -C₁₃H₈)MCl₂ and [3,6-di-*t*Bu-C₁₃H₆SiMe₂NtBu]MCl₂ (M=Hf, Zr or Ti): mechanistic aspects of the catalytic formation of a isotactic-syndiotactic stereoblock-type polypropylene, *J. Organomet. Chem.*, 2001, **621**, 267–276.
- 9 K. Nishii, H. Hagihara, T. Ikeda, M. Akita and T. Shiono, Stereospecific polymerization of propylene with group 4 *ansa*-fluorenylamidodimethyl complexes, *J. Organomet. Chem.*, 2006, **691**, 193–201.
- 10 R. Tanaka, C. Yanase, Z. Cai, Y. Nakayama and T. Shiono, Structure-stereospecificity relationships of propylene polymerization using substituted *ansa*-silylene (fluorenyl)amido titanium complexes, *J. Organomet. Chem.*, 2016, **804**, 95–100.
- 11 H. V. R. Dias and Z. Wang, Syntheses and characterization of zirconium and hafnium complexes of amido-fluorenyl ligands [(NBu^t)SiMe₂CH₂(C₁₃H₈)]²⁻ and [(NPr^t)SiMe₂CH₂(C₁₃H₈)]²⁻, *J. Organomet. Chem.*, 1997, **539**, 77–85.
- 12 W. Wang, S. Qu, X. Li, J.; Chen, Z.; Guo and W.-H. Sun, Transition metal complex catalysts promoting copolymers



- of cycloolefin with propylene/higher olefins, *Coord. Chem. Rev.*, 2023, **494**, 215351.
- 13 H. Yuan, T. Kida, R. Tanaka, Z. Cai, Y. Nakayama, S. Kihara and T. Shiono, Star polymers with norbornene/1-octene gradient copolymer arms synthesized by an *ansa*-fluorenylamidodimethyltitanium- $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ catalyst system, *Polymer*, 2022, **249**, 124844.
 - 14 H. G. Alt and A. Reb, Amido functionalized *ansa*-fluorenylidene half-sandwich complexes of zirconium as catalyst precursors for homogeneous ethylene polymerization, *J. Mol. Catal. A: Chem.*, 2001, **175**, 43–50.
 - 15 R. Tanaka, Y. Nakayama and T. Shiono, Synthesis of high-molecular weight block copolymers of norbornene and propylene with methyl methacrylate initiated by a fluorenylamido titanium complex, *Polym. Chem.*, 2013, **4**, 3974.
 - 16 Z. Cai, T. Ikeda, M. Akita and T. Shiono, Substituent effects of *tert*-butyl groups on fluorenyl ligand in syndiospecific living polymerization of propylene with *ansa*-fluorenylamidodimethyl-titanium complex, *Macromolecules*, 2005, **38**, 8135–8139.
 - 17 Z. Cai, R. Harada, Y. Nakayama and T. Shiono, Highly active living random copolymerization of norbornene and 1-alkene with *ansa*-fluorenylamidodimethyl-titanium derivative: Substituent effects on fluorenyl ligand, *Macromolecules*, 2010, **43**, 4527–4531.
 - 18 T. Hasan, T. Ikeda and T. Shiono, Random copolymerization of propene and norbornene with *ansa*-fluorenylamidodimethyl-titanium-based catalysts, *Macromolecules*, 2005, **38**, 1071–1074.
 - 19 Y.; Sun, C. Wang, R. Tanaka, T. Shiono and Z. Cai, Copolymerization of ethylene and fluoroalkylnorbornene using highly active *ansa*-(fluorenyl)(amido)titanium-based catalysts, *Macromol. Chem. Phys.*, 2019, **220**, 1900306.
 - 20 X. Song, Q. Ma, Z. Cai, R. Tanaka, T. Shiono and R. B. Grubbs, Facile synthesis of novel polyethylene-based A-B-C block copolymers containing poly(methyl methacrylate) using a living polymerization system, *Macromol. Rapid Commun.*, 2016, **37**, 227–231.
 - 21 J. Okuda, F. J. Schattenmann, S. Wocadlo and W. Massa, Synthesis and characterization of zirconium complexes containing a linked amido-fluorenyl ligand, *Organometallics*, 1995, **14**, 789–795.
 - 22 A. Rajesh and S. Sivaram, Polymerization of ethylene using amido functional half-sandwich complexes of group 4 metals, *Polym. Eng. Sci.*, 2011, **51**, 2103–2108.
 - 23 H. Wang, H. Wang, Y. Sun, H.; Cheng, T. Shiono and Z. Cai, Living polymerization of propylene with *ansa*-dimethylsilylene(fluorenyl)(cumylamido) titanium complexes, *Polymers*, 2017, **9**, 131.
 - 24 H. Wang, Y. Li and Z. Cai, Substituent effects of phenyl group on silylene bridge in stereospecific polymerization of propylene with C_1 -symmetric *ansa*-silylene(fluorenyl)(amido) dimethyl titanium complexes, *Polymers*, 2018, **10**, 1075.
 - 25 Y. Sun, B. Xu, T. Shiono and Z. Cai, Highly active *ansa*-(fluorenyl)(amido)titanium-based catalysts with low load of methylaluminoxane for syndiotactic-specific living polymerization of propylene, *Organometallics*, 2017, **36**, 3009–3012.
 - 26 H. Yuan, T. Kida, H. Kim, R. Tanaka, Z. Cai, Y. Nakayama and T. Shiono, Synthesis and properties of gradient copolymers composed of norbornene and higher α -olefins using an *ansa*-fluorenylamidodimethyl-titanium- $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ catalyst system, *Macromolecules*, 2020, **53**, 4323–4329.
 - 27 T. Toda, I. Miura, S. Ohta and K. Takenaka, Synthesis, structural analysis, and polymerization activity of noncyclopentadienyl constrained geometry complex $[\text{Me}_2\text{Si}(\text{Ph}_2\text{C})(\text{tBuN})]\text{ZrCl}_2(\text{thf})$, *Appl. Organomet. Chem.*, 2024, **38**, e7710.
 - 28 L. J. Irwin, J. H. Reibenspies and S. A. Miller, A sterically expanded “Constrained Geometry Catalyst” for highly active olefin polymerization and copolymerization: An unyielding comonomer effect, *J. Am. Chem. Soc.*, 2004, **126**, 16716–16717.
 - 29 L. J. Irwin, J. H. Reibenspies and S. A. Miller, Synthesis and characterization of sterically expanded *ansa*- η^1 -fluorenylamido complexes, *Polyhedron*, 2005, **24**, 1314–1324.
 - 30 E. D. Schwerdtfeger and S. A. Miller, Intrinsic branching effects in syndiotactic copolymers of propylene and higher α -olefins, *Macromolecules*, 2007, **40**, 5662–5668.
 - 31 E. D. Schwerdtfeger, L. J. Irwin and S. A. Miller, Highly branched polyethylene from ethylene alone via a single zirconium-based catalyst, *Macromolecules*, 2008, **41**, 1080–1085.
 - 32 J. Chai, K. A. Abboud and S. A. Miller, Sterically expanded CGC catalysts: Substituent effects on ethylene and α -olefin polymerization, *Dalton Trans.*, 2013, **42**, 9139–9147.
 - 33 J.; Bao, Y.; Li, C.-M. Chan, K.-C. Law, S.-M. Yiu and M. C. W. Chan, Geometrically constrained cofacial bi-titanium olefin polymerization catalysts: Tuning and enhancing comonomer incorporation density, *ACS Catal.*, 2024, **14**, 17911–17918.
 - 34 T. Shiono, Living polymerization of olefins with *ansa*-dimethylsilylene(fluorenyl)(amido) dimethyl-titanium-based catalysts, *Polym. J.*, 2011, **43**, 331–351.
 - 35 P. S. Kulyabin, D. V. Uborsky, A. Z. Voskoboinikov, J. A. M. Canich and J. R. Hagadorn, Pyridylamido hafnium complexes with a silylene bridge: synthesis and olefin polymerization, *Dalton Trans.*, 2020, **49**, 6693–6702.
 - 36 W.; Kaminsky, B. Hinrichs and D. Rehder, Diolefin polymerization by half-sandwich complexes and MAO as cocatalyst, *Polymer*, 2002, 7225–7229.
 - 37 E.; Kirillov, A. Razavi and J.-F. Carpentier, Syndiotactic-enriched propylene–styrene copolymers using fluorenyl-based half-titanocene catalysts, *J. Mol. Catal. A: Chem.*, 2006, 230–235.
 - 38 F. Li and W. Liu, Progress in the catalyst for ethylene/ α -olefin copolymerization at high temperature, *Can. J. Chem. Eng.*, 2023, **101**, 4992–5019.
 - 39 A. Vittoria, G. P. Goryunov, V. V. Izmer, D. S. Kononovich, O. V. Samsonov, F. Zaccaria, G. Urciuoli, P. H. M. Budzelaar, V. Busico, A. Z. Voskoboinikov, D. V. Uborsky, C. Ehm and R. Cipullo, Hafnium vs. zirconium



- nium, the perpetual battle for supremacy in catalytic olefin polymerization: A simple matter of electrophilicity?, *Polymers*, 2021, **13**, 2621.
- 40 Z. Cai, T. Ikeda, M. Akita and T. Shiono, Substituent effects of *tert*-butyl groups on fluorenyl ligand in syndiospecific living polymerization of propylene with *ansa*-fluorenylamidodimethyl-titanium complex, *Macromolecules*, 2005, **38**, 8135–8139.
- 41 F. Song, R. D. Cannon, S. J. Lancaster and M. Bochmann, Activator effects in metallocene-based alkene polymerisations: unexpectedly strong dependence of catalyst activity on trityl-concentration, *J. Mol. Catal. A: Chem.*, 2004, **218**, 21–28.
- 42 C. Ehm, A. Mingione, A. Vittoria, F. Zaccaria, R. Cipullo and V. Busico, High-Throughput Experimentation in Olefin Polymerization Catalysis: Facing the Challenges of Miniaturization, *Ind. Eng. Chem. Res.*, 2020, **59**, 13940–13947.
- 43 V. L. Cruz, A. Muños-Escalona and J. Martinez-Salazar, A theoretical study of the comonomer effect in the ethylene polymerization with zirconocene catalytic systems, *J. Polym. Sci., Part A: Polym. Chem.*, 1998, **36**, 1157–1167.
- 44 C. Gotz, A. Rau and G. Luft, Ternary metallocene catalyst systems based on metallocene dichlorides and $\text{AlBu}^i_3/[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$. NMR investigations of the influence of Al/Zr ratios on alkylation and on formation of the precursor of the active metallocene species, *J. Mol. Catal. A: Chem.*, 2002, **184**, 95–110.
- 45 S. M. Baldwin, J. E. Bercaw, L. M. Henling, M. W. Day and H. H. Brintzinger, Cationic, Alkylaluminum-Complexed Zirconocene Hydrides: NMR-Spectroscopic Identification, Crystallographic Structure Determination, and Interconversion with Other Zirconocene Cations, *J. Am. Chem. Soc.*, 2011, **133**, 1805–1813 and references cited therein.
- 46 H. Knuutila, A. Lehtinen and A. Nummila-Pakarinen, Advanced polyethylene technologies - Controlled material properties, *Adv. Polym. Sci.*, 2004, **169**, 13–27.
- 47 L. Castro, E. Kirillov, O. Miserque, A. Welle, L. Haspeslagh, J.-F. Carpentier and L. Maron, Are solvent and dispersion effects crucial in olefin polymerization DFT calculations? Some insights from propylene coordination and insertion reactions with group 3 and 4 metallocenes, *ACS Catal.*, 2015, **5**, 416–425.
- 48 L. Castro, G. Theurkauff, A. Vantomme, A. Welle, L. Haspeslagh, J.-M. Brusson, L. Maron, J.-F. Carpentier and E. A. Kirillov, Theoretical outlook on the stereoselectivity origins of isoselective zirconocene propylene polymerization Catalysts, *Chem. – Eur. J.*, 2018, **24**, 10784–10792.
- 49 M. Bochmann, The chemistry of catalyst activation: the case of group 4 polymerization catalysts, *Organometallics*, 2010, **29**, 4711–4740.
- 50 E. Y.-X. Chen and T. J. Marks, Cocatalysts for metal-catalyzed olefin polymerization: activators, activation processes, and structure-activity relationships, *Chem. Rev.*, 2000, **100**, 1391–1434.
- 51 G. Theurkauff, A. Bondon, V. Dorcet, J.-F. Carpentier and E. Kirillov, Heterobi- and -trimetallic ion pairs of zirconocene-based isoselective olefin polymerization catalysts with AlMe_3 , *Angew. Chem., Int. Ed.*, 2015, **54**, 6343–6346.
- 52 G. Theurkauff, M. Bader, N. Marquet, A. Bondon, T. Roisnel, J.-P. Guegan, A. Amar, A. Boucekkine, J.-F. Carpentier and E. Kirillov, Discrete ionic complexes of highly isoselective zirconocenes. Solution dynamics, trimethylaluminum adducts, and implications in propylene polymerization, *Organometallics*, 2016, **35**, 258–276.
- 53 X. Desert, P. Proutiere, A. Welle, K. Den Dauw, A. Vantomme, O. Miserque, J.-M. Brusson, J.-F. Carpentier and E. Kirillov, Zirconocene-catalyzed polymerization of α -olefins: When intrinsic higher activity is flawed by rapid deactivation, *Organometallics*, 2019, **38**, 2664–2673.
- 54 X. Desert, J.-F. Carpentier and E. Kirillov, Quantification of active sites in single-site group 4 metal olefin polymerization catalysis, *Coord. Chem. Rev.*, 2019, **386**, 50–68.
- 55 A. Hermann, A. Münch, S. A. Orr, R. Herbst-Irmer, R. E. Mulvey, C. Strohmann and D. Stalke, When electrons step in: Polarizing effects explored with triisobutylaluminum, *Inorg. Chem.*, 2021, **60**, 2872–2877.
- 56 R. G. Vranka and E. L. Amma, Crystal structure of trimethylaluminum, *J. Am. Chem. Soc.*, 1967, **89**, 3121–3126.
- 57 V. Busico, R. Cipullo, R. Pellecchia, G. Talarico and A. Razavi, Hafnocenes and MAO: Beware of trimethylaluminum!, *Macromolecules*, 2009, **42**, 1789–1791.
- 58 (a) CCDC 2497781: Experimental Crystal Structure Determination, 2026, DOI: [10.5517/ccdc.csd.cc2pv4l9](https://doi.org/10.5517/ccdc.csd.cc2pv4l9); (b) CCDC 2497782: Experimental Crystal Structure Determination, 2026, DOI: [10.5517/ccdc.csd.cc2pv4mb](https://doi.org/10.5517/ccdc.csd.cc2pv4mb); (c) CCDC 2497783: Experimental Crystal Structure Determination, 2026, DOI: [10.5517/ccdc.csd.cc2pv4nc](https://doi.org/10.5517/ccdc.csd.cc2pv4nc).

