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Cocatalyst effects in Hf-catalysed olefin polymerization: taking well-defined Al–alkyl borate salts into account†

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Hafnium catalysts for olefin polymerization are often very sensitive to the nature of cocatalysts, especially if they contain "free" aluminium trialkyls. Herein, cocatalyst effects in Hf-catalysed propene polymerization are examined for four Hf catalysts belonging to the family of C_S-symmetric (**Hf-C_S-Met**) and C_2-symmetric (**Hf-C_2-Met**) metallocenes, as well as of octahedral (**Hf-OOOO**) and pentacoordinated (**Hf-PyAm**) "post-metallocenes". The performance of the recently developed $\{[iBu_2(PhNMe_2)Al]_2(\mu\text{-}H)\}^+[B(C_6F_5)_4]^-$ (**AlHAl**) cocatalyst is compared with that of established systems like methylalumoxane, phenol-modified methylalumoxane and trityl borate/tri-iso-butylaluminium. The worst catalytic performance is observed with MAO. Conversely, the best cocatalyst varies depending on the Hf catalyst used and the performance indicator of interest, highlighting the complexity and importance of selecting the right precatalyst/cocatalyst combination. **AlHAl** proved to be a suitable system for all catalysts tested and, in some cases, it provides the best performance in terms of productivity (*e.g.* with hafnocenes). Furthermore, it generally leads to high molecular weight polymers, also with catalysts enabling easy chain transfer to Al like **Hf-PyAm**. This suggests that **AlHAl** has a low tendency to form heterodinuclear adducts with the cationic active species, therefore preventing the formation of dormant sites and/or termination events by chain transfer to Al.

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Introduction

Optimization of molecular catalysts typically implies tailoring of ancillary ligands and/or variation of metal centres for property modulation.[1] Molecular catalysts for olefin polymerization represent a noticeable example in this respect: over the last few decades, tremendous progress in the development of group 4 metallocene[2] and "post-metallocene"[3,4] catalysts has resulted in a large variety of high-performance systems, some of them being currently employed in commercial processes.[5]

The structure of (pre)catalysts, however, is *not* the only variable determining polymerization performance, since activators or – more generally – cocatalysts are an equally important component of the catalytic pool.[6–8] First, productivity is strongly dependent on the nature of the cocatalyst, which determines the effectiveness of precatalyst activation and impurity scavenging, and is often involved in side reactions with the active species.[6–12] Furthermore, the cocatalyst usually provides the cationic active species with a counterion, therefore determining ion pairing interactions[6,13–15] that potentially influence catalytic activity[16–24] and stereoselectivity.[25–29]

An intriguing example of cocatalyst effects concerns Hf catalysts. Hafnocenes, for instance, have long been found to be poorly active and unable to compete with their Zr-based analogues,[30–33] until highly effective cocatalysts other than methylaluminoxane (MAO)[34,35] became readily available in research laboratories. The group of Rieger first demonstrated that hafnocenes and zirconocenes actually show comparable productivity when using, instead of MAO, a binary cocatalyst comprising an alkyl abstractor like $[Ph_3C][B(C_6F_5)_4]$ (trityl borate, TTB) and an alkylating and impurity scavenging agent like tri-iso-butylaluminium (TIBAL).[36] Later studies by the group of Busico revealed that a similar increase in hafnocene productivity can be achieved by using MAO/BHT,[37] that is, a modified MAO in which the residual trimethylaluminium (TMA) component is scavenged by reaction with a sterically

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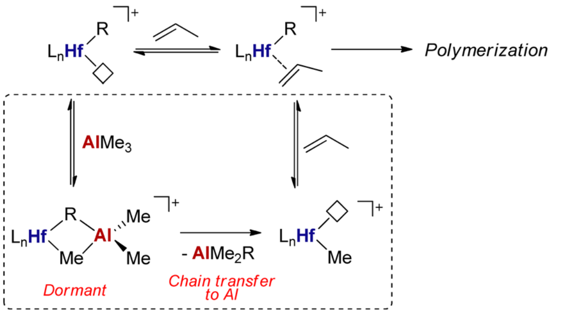
hindered phenol (*i.e.* 2,6-di-*tert*-butyl-4-methylphenol, BHT).[38–41] A significant increase of polymer molecular weights and smaller effects on polymer stereoregularity were also observed.[37]

The cocatalyst sensitivity is therefore attributed to the generally higher tendency of hafnocenes to form Hf/Al heterodinuclear adducts, which represent dormant intermediates and are involved in chain termination events *via* chain transfer to Al (Scheme 1).[12,37,42–45] This is particularly problematic with TMA, while bulkier Al–alkyls like TIBAL are less prone to forming such adducts.[6,8,12]

Recently, we identified an unusual Al–alkyl borate salt (**AlHAl**, Fig. 1), behaving as a single component cocatalyst like MAO but exhibiting a well-defined structure like typical organic borate salts (*e.g.* TTB).[46] Among the desirable properties of this species is the stability of its dinuclear Al–alkyl cation, which features coordinatively saturated aluminium centres possessing "latent" Lewis acidity.[47] **AlHAl** has been tested in combination with representative zirconocene catalysts in propene polymerization in toluene[46] and, upon suitable structural modification, in ethylene/1-hexene copolymerization in hydrocarbon solvents at high temperatures.[48] In both cases, it proved to be competitive with established cocatalysts, offering the advantage of requiring only ∼50 equivalents (or even less) for efficient precatalyst activation and impurity scavenging. It therefore requires orders of magnitude lower Al/Zr ratios compared to MAO (typically on the order of 10^3–10^4).[34]

Owing to the stabilized nature of the Al centres and the low Al/M ratio required (M = group 4 metal), **AlHAl** is expected to exhibit a low tendency to form heteronuclear adducts with transition metal active species, potentially making it suitable for applications with Hf catalysts. Herein, the performance of **AlHAl** is compared with that of established systems such as MAO, MAO/BHT and TTB/TIBAL for representative examples of four classes of Hf-based metallocene and "post-metallocene" catalysts.



Scheme 1 Formation of dormant Hf/Al heterodinuclear adducts and chain transfer to aluminium as potential side reactions in olefin polymerization. L = ancillary ligand; R = methyl or polymeryl.

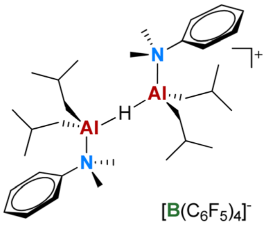


Fig. 1 Structure of the **AlHAl** cocatalyst.[46]

Results and discussion

The four Hf catalysts studied are shown in Fig. 2. They were selected as representative examples of the widely studied classes of C_S- and C_2-symmetric metallocenes, as well as of the less explored families of hexa- and penta-coordinated "post-metallocenes". They include:

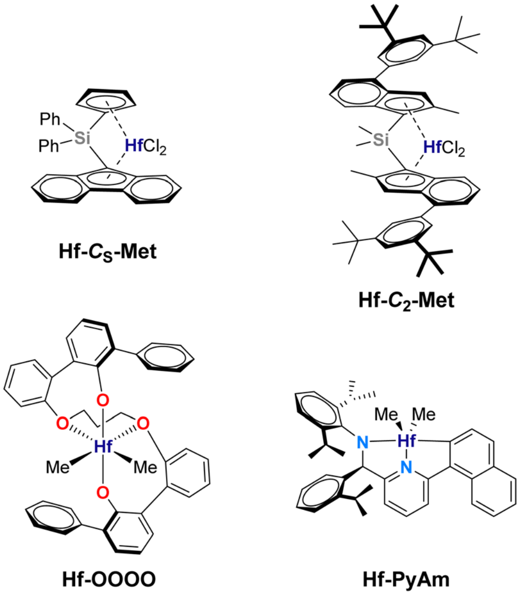
(1) A C_S-symmetric metallocene (**Hf-C_S-Met**), the same that was studied in one of the aforementioned literature papers on cocatalyst effects;[37]

(2) A 2,4-substituted silyl-bis(indenyl) C_2-symmetric metallocene (**Hf-C_2-Met**);[49]

(3) A "post-metallocene" catalyst featuring a tetradentate OOOO–ligand of the type patented by DOW chemicals (**Hf-OOOO**);[50–53]

(4) A pentacoordinated Hf-pyridylamido catalyst of the type used industrially for the production of olefin block copolymers *via* chain shuttling copolymerization (**Hf-PyAm**).[54–56]

These systems were tested in propene polymerization under reaction conditions analogous to those of literature reports,[37] that is, in toluene at moderate pressure (2 bar) and temperature (60 °C). For screening purposes, the concentration of each cocatalyst was fixed at typical values that guarantee efficient impurity scavenging and activating ability, that is, [Al] = 10 mM for MAO and MAO/BHT,[57] 1 mM for TIBAL[57] and



Hf-C_S-Met

Hf-C_2-Met

Hf-OOOO

Hf-PyAm

Fig. 2 Hafnium-based precatalysts studied.

0.1 mM for **AlHAl**.[46,48] Hafnium concentration (4–30 × 10^{-6} M) and reaction time (10–120 min) were varied depending on the productivity of each catalytic system to obtain reasonable polymer yields. Along with productivity, polymer molecular weight and stereoregularity have been selected as performance indicators. The results are summarized in Table 1; variations of performance indicators with respect to MAO are graphically summarized in Fig. 3.

Hf-C_S-Met is the only catalyst of the test set producing syndiotactic polypropylene (sPP), with the other three forming isotactic polypropylene (iPP). The performance of **Hf-C_S-Met** in combination with "classical" cocatalysts (Table 1, entries 1–3) is in reasonably good agreement with literature reports.[37] MAO provides approximately one order of magnitude lower productivity than TTB/TIBAL (0.11 *vs.* 1.6 $kg_{PP}\ mmol_{Cat}^{-1}\ h^{-1}$); only a minor difference is instead observed when comparing MAO/BHT and TTB/TIBAL. Polymer molecular weights follow the same trend, with M_n (kDa) varying as 54 (MAO) < 399 (MAO/BHT) ≈ 411 (TTB/TIBAL): the main chain termination route *via* transfer to aluminium is blocked when using TMA-depleted MAO/BHT or bulky Al–alkyls like TIBAL. Statistical analysis of PP stereosequence distribution by ^{13}C NMR spectroscopy[58] shows that the enantioselectivity of the active sites (σ) remains constant, while the conditional probability of "skipped" monomer insertions (P_{sk}) increases going from MAO to MAO/BHT and TTB/TIBAL, leading to slightly less stereoregular polymers. This can be rationalized considering that the formation of heterodinuclear adducts retards site epimerization (*i.e.* chain relocation without insertion), which is therefore less likely with the TMA-rich MAO cocatalyst.[37]

The new **AlHAl** cocatalyst in comparison provides even better productivity than that observed with TTB/TIBAL (5.5 *vs.* 1.6 $kg_{PP}\ mmol_{Cat}^{-1}\ h^{-1}$, respectively; Table 1, entries 3 and 4). Notably, at the same hafnium concentration used with the other cocatalysts, only 5 equivalents of **AlHAl** (*i.e.* [Al]/[Hf] = 10) suffice for efficient scavenging and catalyst activation. The polymer microstructure is nearly unaffected with respect to the TTB/TIBAL case both in terms of molecular weight and stereoregularity.

Table 1 Summary of propene polymerization results[a]

Entry	Catalyst	[Hf] (10^{-6} M)	Cocatalyst	[Al]/[Hf]	R_p ($kg_{PP}\ mmol_{Cat}^{-1}\ h^{-1}$)	M_n[b] (kDa)	M_w[b] (kDa)	PDI	σ[c]	P_{sk}[d]
1	**Hf-C_S-Met**	20	MAO	500	0.11	54	110	2.0	0.96	0.13
2		20	MAO/BHT	500	1.3	399	877	2.2	0.95	0.20
3		20	TTB/TIBAL	50	1.6	411	970	2.4	0.96	0.21
4		20	**AlHAl**	10	5.5	340	759	2.3	0.95	0.22
5	**Hf-C_2-Met**	30	MAO	333	0.05	91	269	2.9	0.999	
6		30	MAO/BHT	333	0.12	136	397	2.9	0.997	
7		12	TTB/TIBAL	100	3.3	74	168	2.3	0.995	
8		12	**AlHAl**	20	3.2	52	117	2.2	0.993	
9	**Hf-OOOO**	10	MAO	1000	3.6	5.6	22	3.8	0.87	
10		10	MAO/BHT	1000	8.4	299	702	2.3	0.87	
11		10	TTB/TIBAL	100	4.0	31	67	2.2	0.89	
12		10	**AlHAl**	20	3.1	55	125	2.3	0.88	
13	**Hf-PyAm**	4	MAO	750[e]	4.0	11	66	6.1	0.994	
14		4	MAO/BHT	750[e]	27	801	1944	2.4	0.994	
15		4	MAO/BHT	2500	24	678	1586	2.4	0.994	
16		4	TTB/TIBAL	250	24	60	176	2.9	0.994	
17		4	**AlHAl**	50	5.9	296	947	3.2	0.995	

[a] In toluene (5 mL), 60 °C, $p_{propene}$ = 2 bar (30 psi); [Al] = 10 mM for MAO and MAO/BHT, 1 mM for TIBAL or 0.1 mM for **AlHAl**; [B]/[Hf] = 5 for dichloride precatalysts **Hf-C_S-Met** and **Hf-C_2-Met**,[37,49] 1 for **Hf-OOOO**[52] or 2 for **Hf-PyAm**,[59,60] according to previously optimized procedures. [b] As determined by GPC. [c] Probability of inserting propene with the favoured enantioface at each of the two enantiotopic sites. [d] Conditional probability of "skipped insertion". [e] [Al] = 3 mM, see the main text. See also Table S1.†

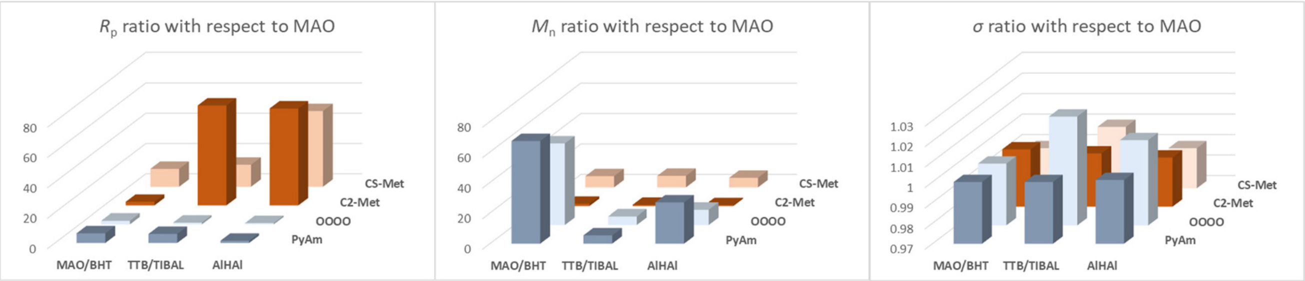


Fig. 3 Variation of productivity (R_p), polymer molecular weight (M_n) and stereoselectivity (σ) with respect to MAO: for each catalyst, variation of each performance parameter is reported as a ratio with respect to polymerization carried out with MAO (see also Table 1).

Also for the isotactic-selective metallocene catalyst screened, **Hf-C_2-Met**, **AlHAl** and TTB/TIBAL are the best performing cocatalysts, providing similar productivity and polymer molecular weights (Table 1, entries 5 and 6; Fig. 3). MAO and MAO/BHT show significantly worse performance: broad polymer molecular weight distributions and very low iPP yields were obtained, even at nearly three times higher catalyst concentration (Table 1, entries 5 and 6). Interestingly, the stereoselectivity of the **Hf-C_2-Met**/MAO system exceeds that previously reported at much higher propene pressure for the same catalyst[49] and even approaches the performance of its Zr analogue[61] in combination with TTB/TIBAL: this further exemplifies the complexity of factors determining the performance of hafnocenes, and especially the differences between Hf- and Zr-based catalysts (the so-called "hafnium effect"[49,62–64]).

For the octahedral "post-metallocene" **Hf-OOOO** (Table 1, entries 9–12), the cocatalyst effect on productivity is significantly smaller than that with the above-discussed metallocenes: maximum variations by a factor of only ∼3, rather than by one to two orders of magnitude, are observed (Fig. 3). MAO/BHT is the best performing cocatalyst in this case (8.4 $\text{kg}_{\text{PP}}\ \text{mmol}_{\text{Cat}}^{-1}\ \text{h}^{-1}$), while **AlHAl** (3.1 $\text{kg}_{\text{PP}}\ \text{mmol}_{\text{Cat}}^{-1}\ \text{h}^{-1}$) performs similar to MAO and TTB/TIBAL. It is however interesting to analyse the kinetic profiles obtained with this catalyst (Fig. 4a). The difference in productivity between MAO and MAO/BHT appears to be solely due to a rather long induction delay observed in the former case (approximately 15 min), after which the slope of the uptake *vs.* time profile becomes nearly identical to that of MAO/BHT. The use of **AlHAl** also leads to an induction delay of approximately 3 min, which is significantly shorter than that with MAO. Polymerization with TTB/TIBAL instead starts very fast and then slows down slightly, up to the point where the slope of the uptake *vs.* time profile tends to become similar to that of **AlHAl**. The long induction delay observed with MAO might be due to the formation of heterodinuclear adducts with TMA retarding chain initiation, and can be prevented by trapping this Al–alkyl with BHT, as previously observed for other catalysts.[9] Also in the case of **AlHAl**, the induction delay has been previously observed in zirconocene-catalysed propene polymerization at higher temperatures and pressures.[46] Although its origin remains to be fully clarified, it is likely due to a milder precatalyst activation reaction by the N-donor stabilized $[\text{AliBu}_2(\text{PhNMe}_2)]^+$ cation[46] compared to that of the "naked" transient $[\text{AliBu}_2]^+$ cation generated by the binary system TTB/TIBAL.[65] Consistently, similar induction delays can be observed also when replacing TTB with $[\text{PhMe}_2\text{NH}][\text{B}(\text{C}_6\text{F}_5)_4]$ (anilinium borate, AB), containing the same aniline ligand present in **AlHAl**.[57] While one would normally prefer fast initiation, these short initial delays can actually be exploited to obtain highly controlled polymerization kinetics also with exceedingly active catalysts, since the reactor conditions can equilibrate after catalyst injection and before polymerization fully begins.[46,57]

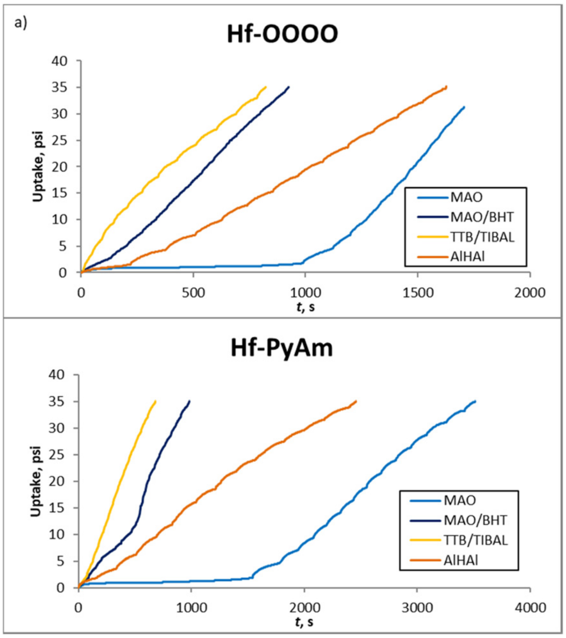


Fig. 4 Selected monomer uptake *vs.* reaction time profiles obtained with (a) **Hf-OOOO** and (b) **Hf-PyAm** in combination with various cocatalysts (see also Fig. S1†).

A marked cocatalyst effect is observed on the molecular weight of polymers produced with **Hf-OOOO**, which follows the trend MAO (M_n = 5.6 kDa) < TTB/TIBAL (31 kDa) < **AlHAl** (55 kDa) ≪ MAO/BHT (299 kDa). Saturated polymer chain ends are observed by NMR spectroscopy, suggesting that this trend can be explained based on the same arguments related to the probability of chain transfer to Al, discussed above for **Hf-C_S-Met**. However, it is important to note here that, with respect to MAO, the molecular weight increases by one order of magnitude when using borate systems, and by almost two orders with MAO/BHT, suggesting that **Hf-OOOO** can have residual interactions even with TIBAL and **AlHAl**-derived Al–alkyls. The stereoselectivity of this catalyst is relatively low: a similar σ of ∼0.87 is observed with the two aluminoxane cocatalysts, which is slightly lower than that with the borate salt-based systems (∼0.89). With such flexible "post-metallocene" catalyst,[50–53] this small difference in stereoselectivity might be ascribed to ion pairing effects on chain epimerization and conformational rearrangements of the cationic active species.[52,66–69]

The last catalyst studied, namely **Hf-PyAm** (Table 1, entries 13–17), is generally quite sensitive to the nature of the cocatalyst, since its rather open active pocket and reactive Hf–aryl bond make it particularly prone to interact/react with all other components of the catalytic pool.[70–73] Chain transfer reactions *via* the formation of heterodinuclear adducts are known to be particularly easy with this catalyst, and represent the main chain termination route even in combination with bulky TIBAL.[54,56,72–76] Since TMA is known to be particularly detrimental to catalytic performance, polymerization in the presence of MAO was here conducted at a lower [Al] of 3 mM (*i.e.* Al/Hf = 750); the performance of the MAO/BHT system is nearly the same at [Al] = 3 or 10 mM (Table 1, entries 13–15).

In terms of productivity, MAO/BHT and TTB/TIBAL are the best performing systems for **Hf-PyAm**, with a similar R_p of ~24 kg_{PP} $mmol_{Cat}^{-1}$ h^{-1}, which is approximately six times higher than that with MAO (Fig. 3); also in this case, a very long induction delay of ~25 min contributes towards making the MAO-activated system less productive (Fig. 4b). **AlHAl** exhibits only a slightly better performance than MAO in terms of averaged productivity (5.9 *vs.* 4.0 kg_{PP} $mmol_{Cat}^{-1}$ h^{-1}).

The relatively low productivity observed with MAO can be explained based on the ease of formation of dormant heterodinuclear adducts and of side reactions involving the Hf–aryl bond with residual TMA.[72,73] This might explain also the low M_n and broad molecular weight distributions observed with this cocatalyst (PDI = 6.1).

Although no conclusive explanation can be drawn, it is instructive to analyse also the possible origins of the somewhat poor performance of **AlHAl**. The same explanation proposed for MAO hardly applies here: as discussed above, the Al-compounds derived from **AlHAl** are expected to be less interactive with the active species than TMA. In fact, the polymer molecular weight observed with this cocatalyst ($M_n \approx 300$ kDa) is significantly higher than that with MAO and even TTB/TIBAL (11 and 60 kDa, respectively), and it is on the same order of magnitude of the highest one obtained with MAO/BHT (~700–800 kDa; Fig. 3): this indicates a very low tendency of **AlHAl** to trigger chain termination by chain transfer to Al even with **Hf-PyAm**. Ineffective precatalyst activation is also an unlikely explanation since simple methyl abstraction is required with a dimethyl precatalyst like **Hf-PyAm**. The difference in productivity is therefore likely related to other types of side reactions. For instance, it has been previously shown that the easily accessible Hf-active sites of **Hf-PyAm** might be poisoned by the dimethylaniline ligand of AB,[71,77] which is the same as that present in **AlHAl**. Double methyl abstraction in the presence of a relatively large excess of cationic and highly Lewis acidic Al–alkyl species might be another possibility.[78,79]

No cocatalyst effect is observed on the stereoselectivity of **Hf-PyAm**, which provides highly isotactic PP, as expected.[55,80,81]

Conclusions

The performance in propene polymerization of four representative metallocene and "post-metallocene" Hf catalysts has been explored in combination with various cocatalysts, namely MAO, MAO/BHT, TTB/TIBAL and the recently developed **AlHAl**. Cocatalyst effects of variable intensity have been observed (Fig. 3). The productivity of the metallocene catalysts **Hf-*C*$_S$-Met** and **Hf-*C*$_2$-Met** depends strongly on the cocatalyst nature, while variations are more moderate for **Hf-PyAm** and **Hf-OOOO**. The polymer molecular weight exhibits a large variability for all catalysts except **Hf-*C*$_2$-Met**, while cocatalyst effects on stereoselectivity are smaller.

MAO is generally the worst performing system, likely due to the side reactions involving its TMA component. Conversely, identifying the best cocatalyst for the whole set of Hf catalysts is not straightforward. MAO/BHT generally provides the highest polymer molecular weight; furthermore, it leads to the highest productivity with the "post-metallocene" catalysts **Hf-OOOO** and **Hf-PyAm**, while being rather ineffective in activating the metallocene **Hf-*C*$_2$-Met**. Similarly, TTB/TIBAL provides quite high productivities in all cases, but it leads to easy chain transfer to Al with the two "post-metallocenes".

Notably, **AlHAl** appears to be comparable with the established cocatalysts. In terms of productivity, it provides the best performance with the two metallocene catalysts and, although it performs worse with **Hf-OOOO** and **Hf-PyAm**, productivity is at most 5-fold lower than that with MAO/BHT. Polymer molecular weights are always similar (*e.g.* with **Hf-*C*$_2$-Met** and **Hf-OOOO**) or even higher (*e.g.* with **Hf-PyAm**) than those obtained with TTB/TIBAL, and sometimes comparable to those obtained with MAO/BHT (**Hf-*C*$_S$-Met**); this indicates that **AlHAl** exhibits a very low tendency to induce chain termination *via* chain transfer to aluminium.

These results therefore provide some more insight into the complexity of cocatalyst effects in Hf-catalysed olefin polymerization. Furthermore, they show that **AlHAl** represents a promising addition to the toolbox of currently available cocatalysts: it is broadly applicable with metallocene and "post-metallocene" catalysts, and it can be successfully employed in cases where chain transfer to aluminium is undesirable, including with catalysts enabling very easy transalkylation like **Hf-PyAm**.

Experimental part

Materials and methods

All manipulations of air-sensitive compounds were conducted under argon or nitrogen using Schlenk techniques and/or MBraun LabMaster 130 glove boxes. **Hf-*C*$_S$-Met** (MCAT), MAO (Lanxess), BHT (Merck), TIBAL (Lanxess), and TTB (Acros) were purchased and used as received. Toluene (Romil) was purchased and purified by passing it through a mixed-bed activated Cu/4 Å molecular-sieve column in an MBraun SPS-5 unit (final concentration of O_2 and H_2O < 1 ppm). Propene (Linde) was purchased and purified by passing it through a mixed-bed activated-Cu/4 Å molecular-sieve column. **Hf-*C*$_2$-Met**,[49] **Hf-OOOO**,[52,53] **Hf-PyAm**[80] and **AlHAl**[46] were synthesized according to literature procedures.

Polymerization experiments

Propene polymerization experiments were performed in a Freeslate (formerly Symyx) parallel pressure reactor setup with 48 reaction cells (PPR48), fully contained in a triple MBraun glovebox operating under nitrogen. The cells, each with a liquid working volume of 5.0 mL, feature an 800 rpm magnetically coupled stirring, and individual online reading/control of the temperature, pressure, monomer uptake, and monomer uptake rate. Experiments were carried out according to established experimental protocols[57,82–84] under reaction conditions used in previous literature reports on Hf catalysts,[37] but without pre-contacting precatalysts and cocatalysts prior to injection into the reactors. All experiments were performed at least in duplicate. A detailed experimental procedure is reported in the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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