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Hafnocenes and MAO: Beware of Trimethylaluminum!

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Revolutionary in the 1980s, group 4 metallocene catalysts for olefin polymerization[1−3] are now becoming mature. The stream of new precatalyst structures has slowed down, and industrial research focuses more and more on technology and application issues.[4] Market penetration, however, has reached a significant level for ethene-based polymers only, whereas it is marginal for propene-based ones due to the persisting domination of the classical Ziegler−Natta systems.[5]

A notable exception is highly syndiotactic polypropylene (sPP), which can only be obtained with C_s-symmetric *ansa*-metallocene catalysts. Compared with the wealth of C_2-symmetric and C_1-symmetric metallocene frameworks, C_s-symmetric ones are more limited,[1−3,6] and most of them are elaborations of the basic structures shown in Chart 1.[7,8] In particular, the 15-year-old zirconocenes **1** and **2**[8] in combination with methylalumoxane (MAO) can still be regarded as plausible standards against which new complexes can be tested. As is common with metallocene catalysts,[1] the Hf(IV)-based homologues **3** and **4** yield polymers with much higher average molecular masses ($\sim$10-fold for polymerizations in bulk propene), albeit at a much lower (ca. 10-fold) rate.[8]

The poor catalytic activity of hafnocenes in general has long been attributed to an inherently low chain propagation constant, until Rieger and co-workers recently showed[9] that with certain C_2-symmetric and C_1-symmetric hafnocenes very high polymerization rates in propene polymerization can be achieved when dimethyl precursors are activated with $[Ph_3C][B(C_6F_5)_4]$ rather than dichloride precursors with MAO (which is the common route). These authors concluded that "*the low activity is not an intrinsic property of Hf(IV)-based catalysts, but results most probably from a slow and inefficient activation through MAO*".

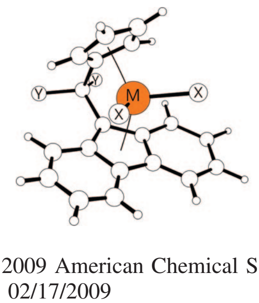
In order to better understand the chemical basis of such finding, we decided to evaluate more carefully the behavior of **3** and **4**, comparatively with **1**, in propene polymerization (T = 60 °C, toluene solvent, $[C_3H_6]$ = 0.75 M) with different activators.[10] A first set of experiments were carried out using MAO or $[Ph_3C][B(C_6F_5)_4]$/Al(*iso*-butyl)$_3$ (TrB/TIBA); as is well-known, TIBA functions as a scavenger and also as a convenient alkylating agent of metallocene dichlorides.[10] The observed productivities are reported in Table 1; compared with zirconocene **1** (entry 1), the two hafnocenes **3** and **4** performed very poorly with MAO (entries 4 and 7), whereas *all three* metallocenes exhibited *very high* productivities upon activation with TrB/TIBA (entries 2, 5, and 8). This confirms Rieger's finding[9] that Zr- and Hf-based catalysts can have similar activities but also demonstrates that MAO activation is detrimental to both Hf dichlorides and Hf dimethyls, which implies that the problem is *not* the alkylation step (at least in the case considered here).

It should be recalled at this point that commercial solutions of MAO always contain significant amounts of "free" $AlMe_3$ (TMA) and that with metallocene cations the latter can form Me-bridged adducts which are believed to be catalytically inactive.[10,11] It has been demonstrated[11] that a practical and highly effective method to scavenge this TMA is to react it in situ with a sterically hindered phenol like 2,6-di-*tert*-butylphenol (TBP); a mole ratio of 2 between TBP and TMA is advisable, to yield the stable and "noninteracting" Al(Me)(2,6-di-*tert*-butylphenoxide)$_2$.[11,12] The results of **1**, **3**, and **4** activation with MAO/TBP, given at entries 3, 6, and 9 of Table 1, are truly impressive: compared with the case of unmodified MAO (entries 1, 4, and 7), catalyst productivity underwent a 4-fold increase for the zirconocene and was boosted by a factor $\sim$35 for the two hafnocenes, thus approaching the performance with TrB/TIBA.

The sPP samples were characterized by GPC and by ^{1}H and ^{13}C NMR (Table 1 and Supporting Information). In agreement with the previous literature,[8] we found that the average molecular weights of the polymers produced with **1** were much lower than those of the homologous samples made with **3** and **4**. On the basis of ^{1}H NMR chain end analysis, we concluded that this is mainly due to faster chain transfer via β-H elimination; terminal vinylidene unsaturations, in fact, were well visible in the former polymers, barely detectable instead in the latter. Compared with unmodified MAO, for all three catalysts activation with MAO/TBP and TrB/TIBA resulted into an increase of polymer molecular weight, which can be traced to the suppression of chain transfer via trans-alkylation with TMA.[11]

The ^{13}C NMR stereosequence distribution (Supporting Information) was subjected to statistical analysis[13] for the determination of the enantioselectivity of the active sites (σ) and of the conditional probability of "skipped" monomer insertions (P_{sk}), i.e., of two consecutive insertion events at the same active site, resulting in the formation of a diagnostic...*rrrrmrrrr*... stereodefect;[1−3,6−8,13,14] the results are also shown in Table 1. Ceteris paribus, the polymers made with **1** were found to be more stereoregular than those made with **3** and **4** (identical within the experimental uncertainty), mainly due to a lower P_{sk}. Given the catalyst, P_{sk} was lower with MAO (with and without added TBP, vide infra) than with TrB/TIBA, particularly for **3** and **4**. A modulation of P_{sk} by ion-pairing interactions for C_s-symmetric metallocene species has been documented before[10,15,16] and traced to the ability of the anion to occupy the coordination vacancy at the transition metal generated by a Cossee-type chain migratory insertion, thus slowing down chain

Chart 1



(1) M = Zr, X = Cl, Y = Ph
(2) M = Zr, X = Me, Y = Ph
(3) M = Hf, X = Cl, Y = Ph
(4) M = Hf, X = Me, Y = Ph
(5) M = Zr, X = Cl or R, Y = Me
(6) M = Hf, X = Cl or R, Y = Me

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Table 1. Results of Propene Polymerization and of sPP Characterization

entry	precatalyst	activator	productivity[a]	M_w, MDa	[*rrrr*][b]	σ[c]	P_{sk}[d]
1	**1**	MAO	2.40	0.11	0.742	0.98	0.050
2		TrB/TIBA	8.40	0.17	0.657	0.97	0.067
3		MAO/TBP	9.68	0.15	0.739	0.98	0.048
4	**3**	MAO	0.06	0.7	0.645	0.97	0.071
5		TrB/TIBA	6.68	1.6	0.319	0.94	0.196
6		MAO/TBP	2.03	1.5	0.454	0.95	0.128
7	**4**	MAO	0.08	0.9	0.628	0.97	0.067
8		TrB/TIBA	6.30	>2	0.294	0.94	0.218
9		MAO/TBP	2.63	>2	0.479	0.95	0.114

[a] In $kg_{PP}\ mmol_M^{-1}\ h^{-1}$. [b] Normalized fraction of syndiotactic pentad. [c] Probability of inserting propene with the favored enantioface at each of the two enantiotopic sites. [d] Conditional probability of "skipped insertions".

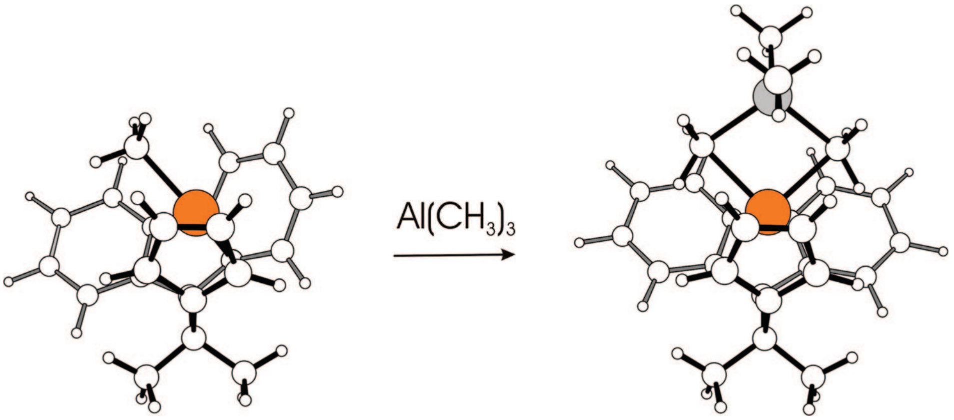

Figure 1. DFT structure of $[Me_2C(Cp)(Flu)M-(\mu\text{-}Me)_2-AlMe_2]^+$.

relocation (site epimerization). In this respect, on the basis of the data in Table 1 the (ill-defined) anion of MAO seems to be more effective than $[B(C_6F_5)_4]^-$ probably because it is slightly more coordinating, specially to Hf; this may explain the residual difference in productivity of **3** and **4** with MAO/TBP and TrB/TIBA.[17] Notably, MAO modification with TBP had limited impact on polymer microstructure (practically no effect for zirconocene **1** and only a moderate increase of P_{sk} for hafnocenes **3** and **4**).

Our interpretation of the above results is that TMA binds to the methyl cations of **3** and **4** much more strongly than to that of **1** and that its inhibiting effect in propene polymerization is correspondingly much higher. To validate this educated guess, we modeled by means of DFT the association of a TMA molecule to active monomethyl cations of **5** and **6** in Chart 1 (eq 1 and Figure 1; for computational details see Supporting Information). As expected, the process was calculated to be highly exothermic, with ΔH values of -26.4 kcal mol^{-1} for **5** and -29.4 kcal mol^{-1} for **6**.

$$[Me_2C(Cp)(Flu)M-Me]^+ + AlMe_3 \rightarrow [Me_2C(Cp)(Flu)M-(\mu\text{-}Me)_2-AlMe_2]^+ \quad (1)$$

Without attaching too much significance to the absolute values of binding energy (solvent and counterion effects having been neglected in the calculations), one should rather note that the hetero-bimetallic bridged species of Figure 1 is more stable by 3.0 kcal mol^{-1} for M = Hf relative to M = Zr. This difference can be very significant in a system characterized by multiple equilibria[10,18] and is likely to result into a much larger pool of "dormant" Hf-(μ-Me)$_2$-Al species compared with the Zr case. Newly published independent solution NMR studies by Bochmann and co-workers are in full agreement with the above interpretation.[19]

The very limited impact of TMA on the stereoselectivity of the propagating species suggests that the formation of $M-(\mu\text{-}P_n)(\mu\text{-}Me)-AlMe_2]^+$ species (P_n = polymeryl), which does occur because it is an intermediate in trans-alkylation,[20] is occasional and labile, as can be expected in view of the low bridging ability of β-branched alkyl residues.[18] This was also confirmed by DFT; indeed, for the process of eq 2 (the isobutyl residue mimicking a growing polypropylene chain) we calculated ΔH values of only -15.4 kcal mol^{-1} for **5** and -18.2 kcal mol^{-1} for **6**.

$$[Me_2C(Cp)(Flu)M-(iso\text{-}Bu)]^+ + AlMe_3 \rightarrow [Me_2C(Cp)(Flu)M-(\mu\text{-}Me)(\mu\text{-}iso\text{-}Bu)-AlMe_2]^+ \quad (2)$$

All in all, the results presented in this Communication highlight a hidden layer of complexity underneath the seemingly straightforward picture of propene polymerization mediated by group 4 metallocene catalysts. In the first place, they demonstrate that catalyst behavior is strongly idiosyncratic and that changing the transition metal from Zr(IV) to Hf(IV) (both d^0 and with practically equal radii) in an otherwise identical ligand framework can alter dramatically—and to a large extent unpredictably—the catalytic performance in practically all respects. A second point is that the ill-defined molecular structure is neither the only nor the principal complication of MAO; in fact, much more important in view of application (at least in the homogeneous phase) is the detrimental effect of "free" TMA in equilibrium with the oligomeric part, which can be overwhelming in cases like the one investigated here. Last but not least, the importance of a proper choice of the anion to optimize the catalytic behavior is not yet fully appreciated and mastered. In particular, achieving the strict kinetic quench propagation regime[21] with regular chain migration which is a prerequisite for highly syndiotactic chain propagation at a C_s-symmetric active species turned out to be, ceteris paribus, more difficult for Hf-based catalysts than for Zr-based ones, which is unfortunate considering the otherwise superior performance of the former. We can only conclude that there is still much to understand and to improve in this “mature” catalysis.[22]

Supporting Information Available: Text giving detailed experimental procedures (propene polymerization, NMR polypropylene characterization, GPC polypropylene characterizations) and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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