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Electronic Effect Rate Enhancement in the Stereoselective Living Coordinative Polymerization of α-Olefins by α,α,α-Trifluoroacetamidinate-Modified Group 4 Metal CPAM^{CF3} Initiators

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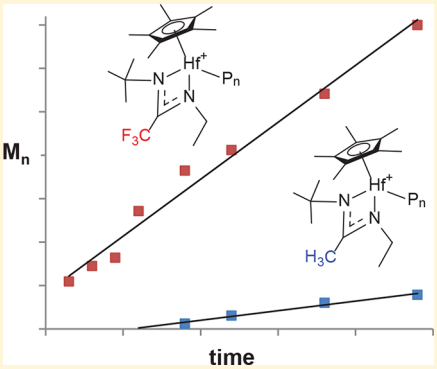
Supporting Information

ABSTRACT: The C_1-symmetric cyclopentadienyl, α,α,α-trifluoroacetamidinate (CPAM^{CF3}) group 4 metal dimethyl complexes, Cp*[N(Et)C(CF_3)N(^{t}Bu)]M-$(Me)_2$ (Cp* = η^5-C_5Me_5) for M = Zr (**3**) and Hf (**4**), serve as initiators for the stereoselective (*isotactic*) living coordination polymerization (LCP) of α-olefins upon in situ "activation" using one equiv of the borate co-initiator, [$PhNMe_2H$]-[$B(C_6F_5)_4$]. For the LCP of 1-hexene using **4**, a six-fold enhancement in the rate of polymerization, R_p, is observed relative to the LCP of this same α-olefin when the nonfluorinated CPAM^{CH3} structural analogue, Cp*[N(Et)C(CH_3)N(^{t}Bu)Hf-$(Me)_2$] (**2**), is employed as the preinitiator. For the LCP of propene, an eight-fold increase in R_p using the CPAM^{CF3} preinitiator **4** now permits production of practical quantities of highly stereo- and regioregular isotactic polypropene (iPP) under reaction conditions that are not amenable for use with the corresponding CPAM^{CH3} preinitiator **2**. These results provide strong support for a unique synergistic coupling of steric and electronic effects of the CPAM^{CF3} ligand environment.



Polyolefins, with a global production volume of over 200 million metric tons per year, easily rank as one of the most important synthetic materials ever devised in terms of the range of technologies and applications currently supported. Nonetheless, the existing profusion of different polyolefin products that are now available can conceivably be expanded upon even further through the design and implementation of new paradigms for olefin polymerization catalysts and reaction processes.[1] Herein, we now report the successful results of an effort to introduce electronic effects associated with the α,α,α-trifluoroacetamidinate ligand into the known family of cyclopentadienyl, amidinate (CPAM) group 4 metal complexes, {(η^5-C_5R_5)[N(R^1)C(X)N(R^2)]M(Me)}[B] (M = Zr or Hf, B = [$B(C_6F_5)_4$] or [$MeB(C_6F_5)_3$]) (**I**), as a means by which to favorably enhance performance as initiators for the stereoselective living coordinative polymerization (LCP) and, by future extension, to the living coordinative chain transfer polymerization (LCCTP) of ethene, propene, higher carbon-numbered α-olefins, and α,ω-nonconjugated dienes.[2,3]

Over the past 20 years, the development and optimization of different derivatives of **I** for use in the (stereoselective) LCP and LCCTP of olefins has relied exclusively on the manipulation of the magnitude of nonbonded steric interactions between substituents within the CPAM ligand environment that also includes those of the growing polyolefin chain.[2a,c−g,3a,d] For these polymerizations, the ion pair **I** is generated in situ from the corresponding CPAM dimethyl preinitiator, (η^5-C_5R_5)[N(R^1)C(X)N(R^2)]M$(Me)_2$ (**II**), through either methyl group protonolysis with the dimethylanilinium borate, [$PhNMe_2(H)$] [$B(C_6F_5)_4$], or abstraction by the trityl borate, [Ph_3C][$B(C_6F_5)_4$], or borane, $B(C_6F_5)_3$. Surprisingly, however, after all these efforts, to date, the best derivative of **II** for achieving the highest degree of stereoselectivity in the LCP of α-olefins still remains the originally reported C_1-symmetric complexes, Cp*[N(Et)C(Me)N(^{t}Bu)]-$M(Me)_2$ (Cp* = η^5- C_5Me_5,) for M = Zr (**1**) and Hf (**2**), that are shown in Scheme 1. With both of these preinitiators, the LCP of 1-hexene proceeds in a stereospecific and 1,2-regiospecific fashion to provide isotactic poly(1-hexene) (iPH).[2a,f] In the case of propene, **1** and **2** also produce isotactic polypropene (iPP) with a degree of enantiosite selectivity for propagation, α, of 0.94, which translates into a stereochemical pentad *mmmm* value of 0.71 as established through a ^{13}C NMR microstructural analysis.[4,5] However, although Zr-based **1** delivers this iPP with up to 3% of 2,1-regioerrors, the corresponding material obtained using the third-row congener **2** is more crystalline and with a higher melting temperature, T_m, by virtue of propagation now having occurred in a regiospecific manner.[6] Unfortunately, with **2**, the observed rate of polymerization, R_p, of α-olefins is 60-times slower than that when **1** is employed under otherwise identical conditions,[2f] and it is this Achilles Heel of the Hf-based system

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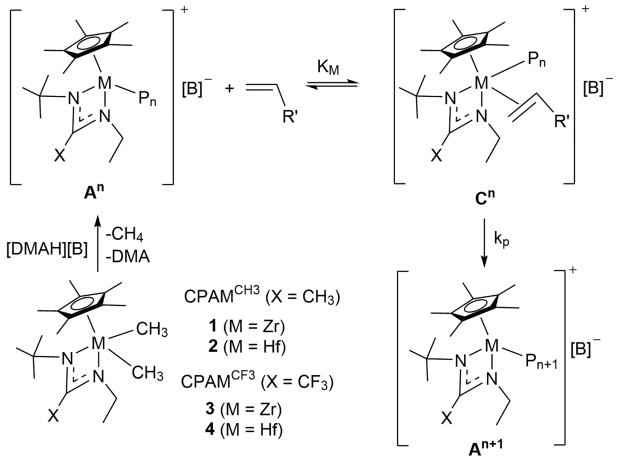
Scheme 1



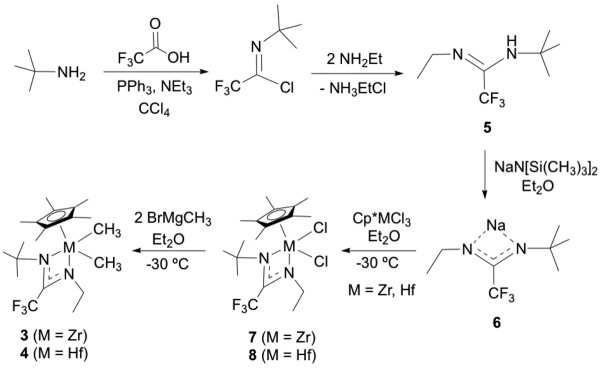
that severely limits its utility to provide practical quantities of a desired polyolefin product by LCP.

Since further optimization of **I** using steric effects alone had largely reached an impasse, we sought to introduce electronic effects into the CPAM ligand set as a way to gain further polymerization performance in terms of enhanced R_p, and potentially, higher degrees of stereo- and regioselectivity as well. For this purpose, placement of a formal electron-withdrawing CF_3 group in the distal position of the amidinate ligand seemed to be a reasonable choice based on the simple, but apparently not previously proposed or pursued, hypothesis that an increase in the electrophilicity of the transition-metal center could serve to shift the equilibrium between the active propagating species, $\mathbf{A}^n$, and the olefin monomer in favor of formation of the π-olefin complex, $\mathbf{C}^n$, that is required for chain growth propagation through migratory insertion according to Scheme 1.[7−9] On the other hand, an increase in transition-metal electrophilicity could also give rise to "tighter" ion pairing within both **I** and $\mathbf{A}^n$ that manifests as slower rates of initiation and propagation, or in the extreme, no polymerization activity at all.[10] Placement of a CF_3 group within the CPAM ligand environment might also have unintended consequences for the LCP of olefins, both negative and positive, through possible introduction of new metal−fluorine and hydrogen−fluorine secondary bonding interactions.[11] Finally, it is recognized at the outset that the CF_3 group is sterically noninnocent, and, in fact, it has been assessed to being equivalent in size to an isopropyl substituent.[12] Since we have previously shown that both the magnitude of R_p and degree of stereoselectivity in the LCP of α-olefins are attenuated by an increase in the steric bulk of the distal X-substituent of the amidinate ligand in **I**,[2e] it is conceivable that the proposed strategy based on Scheme 1 could potentially backfire and actually lead to a less desirable overall polymerization performance.

In practice, the main challenge initially encountered in pursuing an experimental validation of our new strategy with $CPAM^{CF3}$ derivatives of **I** and **II** (X = CF_3) was the absence in the literature of any report whatsoever detailing the synthesis and characterization of lanthanide, transition-metal, or main-group metal complexes supported by an α,α,α-trifluoroacetamidinate ligand, and this includes examples of alkali metal α,α,α-trifluoroacetamidinate salts, $[N(R^1)C(CF_3)N(R^2)][M]$ (where M = Li, Na, or K), that could potentially serve as key reagents.[13] Indeed, in the only report of an α,α,α-trifluoroacetamidine transition-metal complex, the sterically encumbered amidine ligand, N(H)(Ar)C(CF_3)N(Ar) [Ar = 2,6-$(iPr)_2C_6H_3$], is actually coordinated in η^6-arene fashion to a $Mo(CO)_3$ fragment rather than through metal−nitrogen bonds.[14] Finally, this literature survey revealed that, in general, synthetic methods that can be used to access a range of symmetric and unsymmetric α,α,α-trifluororoacetamidines, $N(H)(R^1)C(CF_3)N(R^2)$, have remained largely undeveloped.[15]

Scheme 2 summarizes the synthetic routes used in the present work to prepare the desired new $CPAM^{CF3}$

Scheme 2



preinitiators, $Cp^*[N(^tBu)C(CF_3)N(Et)]M(Me)_2$ for M = Zr (**3**) and Hf (**4**).[16] To begin, synthesis of the unsymmetric CF_3-amidine, $[N(^tBu)C(CF_3)N(H)(Et)]$ (**5**), was achieved through a two-step procedure involving a trifluoroacetimidoyl chloride intermediate according to the procedure of Uneyama and co-workers.[15] Deprotonation of **5** was then accomplished through addition of a slight stoichiometric excess of sodium hexamethyldisilazide, $[NaN(SiMe_3)_2]$, to a diethyl ether (Et_2O) solution to provide the etherate complex, $[N(^tBu)C(CF_3)N(Et)][Na(OEt_2)]$ (**6**), as an analytically pure, dark-red crystalline material after removal of the volatiles and recrystallization of the crude material from pentane at −30 °C.[16] A single-crystal X-ray analysis of **6** revealed the polymeric solid-state structure shown in Figure 1a that is composed of a linear chain of amidinate units that are connected through a repeating intermolecular Na1−N1 bond of 2.420(2) Å. Additional intramolecular Na1−N2, Na1−F3, and Na1−O1 bonding interactions of 2.383(2) Å, 2.362(17) Å, and 2.374(2) Å, respectively, complete the coordination sphere about the Na cation.

As Scheme 2 further presents, synthesis of the required $CPAM^{CF3}$ second- and third-row group 4 metal dichlorides, $Cp^*[N(^tBu)C(CF_3)N(Et)]M(Cl)_2$, where M = Zr (**7**) and Hf (**8**), was accomplished through addition of a stoichiometric equivalent of *in situ*-generated **6** to the corresponding Cp^*MCl_3 starting materials in Et_2O.[16] Both **7** and **8** were isolated as crystalline materials, and X-ray crystallography served to confirm that the CF_3-amidinate ligand coordinates to the group 4 metal in a κ-*N*,*N*′-bidentate fashion. This solid-state molecular structure of **8** is shown in Figure 1b, while that for **7** is presented in the Supporting Information. These data also provide the opportunity to assess the magnitude of the steric impact that the distal CF_3 group has on the overall

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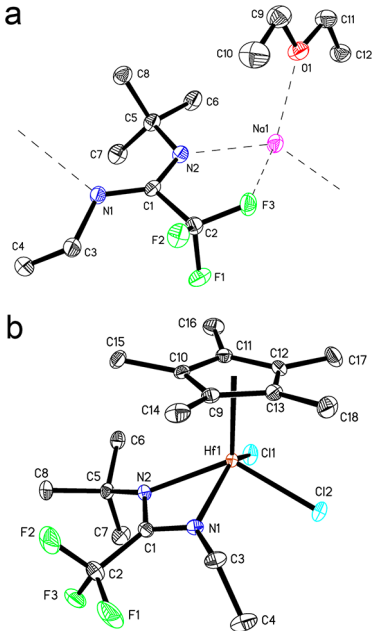

Figure 1. Molecular structures (30% thermal ellipsoids) of (a) **6** and (b) **8**. Hydrogen atoms have been removed for the sake of clarity.

CPAM^{CF3} ligand sphere about the transition-metal center. For this purpose, Table 1 presents selected bond angles for **7** and **8**

Table 1. Selected Bond Angles for Cp*[N(^{t}Bu)C(X)N(Et)]M(Y)$_2$

X, M, Y	M−N−C_{tBu} (deg)	M−N−C_{Et} (deg)
tBu, Zr Cl	136.6(2)	131.4(2)
CF_3, Zr, Cl (**7**)	137.10(7)	133.33(8)
CF_3, Hf, Cl (**8**)	137.5(1)	133.3(1)
Ph, Zr, Cl	140.6(2)	140.4(2)
H, Zr, Cl	146.40(9)	145.64(16)
tBu, Zr, CH_3	135.1(3)	132.7(3)
CH_3, Hf, CH_3	139.9(3)	138.6(3)
CH_3, Zr, CH_3	142.5(16)	136.4(17)
H, Zr, CH_3	147.30(7)	141.20(8)

along with corresponding values for a series of closely related CPAM^X group 4 metal dichloride and dimethyl analogues.[2,3] As can be seen, the M−N−C_{tBu} and M−N−C_{Et} bond angles are highly sensitive to the magnitude of "buttressing" interactions between the distal X substituent and the *N*-^{t}Bu and *N*-ethyl groups of the amidinate ligand that help to define the extent of steric crowding about the transition-metal center. Of significant importance to the current study is the observation that the distal CF_3 group of **7** and **8** appears to have a steric impact within the CPAM ligand sphere that lies somewhere between those manifested by distal Ph and ^{t}Bu groups and is significantly larger than that of distal CH_3 and H substituents.

As a final synthetic consideration, Scheme 2 confirms that the desired group 4 CPAM^{CF3} dimethyl preinitiators, **3** and **4**, could be prepared through methylation of **7** and **8**, respectively, using two equivalents of methyl magnesium bromide. Unfortunately, unlike their dichloride precursors, both **3** and **4** were found to exist as very viscous, yellow oils that tend to retain solvent tightly, and as such, confirmation of molecular structure could not be unequivocally confirmed by X-ray crystallography, nor was it possible to obtain a satisfactory elemental analysis in each case. On the other hand, a high degree of chemical purity (>95%) was established for both **3** and **4** through ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy.[16] Interestingly, ^{1}H NMR (400 MHz, benzene-d_6, 25 °C) spectra of both **3** and **4** display a well-defined long-range $^5J(^1H-^{19}F)$ coupling constant of 2.4 Hz between the distal CF_3 group and the methylene (CH_2) unit of the *N*-Et substituent. Furthermore, in keeping with other derivatives of **I**, only a single ^{1}H resonance is observed for the two diastereotopic M-Me groups in the ^{1}H NMR spectra of **3** and **4**, and a preliminary variable-temperature ^{1}H NMR investigation of the latter confirmed that rapid metal-centered racemization occurs through an intramolecular "amidinate ring-flipping" process that has an associated free energy of activation, $\Delta G^{\ddagger}$, of <10 kcal mol^{-1} at the coalescence temperature, T_c, of 243 K according to an Eyring analysis. Surprisingly, this $\Delta G^{\ddagger}$ value for the CPAM^{CF3} derivative **4** closely matches in magnitude that established for the CPAM^{CH3} analogue **2**.[2a]

As further proof of structure and composition, both **3** and **4** indeed proved capable of serving as preinitiators for the stereoselective LCP of 1-hexene and propene. However, because of the higher level of spectroscopically confirmed purity that could be routinely obtained for **4**, the preliminary LCP studies reported herein were performed using this CPAM^{CF3} preinitiator. Thus, addition of 200 equiv of 1-hexene to the clear yellow "initiator" solution formed from prior addition of 1 equiv of [PhNMe$_2$H][B(C$_6$F$_4$)$_4$] to **4** in chlorobenzene (PhCl) at −10 °C, provided an excellent yield of iPH after a 10 h polymerization time and the usual workup.[16] Analytical characterization of this iPH material by gel permeation chromatography (GPC) gave number-average and weight-average molecular weight indices, M_n and M_w, of 18.2 kDa and 18.5 kDa, respectively, which together establish a polydispersity $Đ$ value of 1.02. A ^{1}H NMR (800 MHz, 1,1,2,2-CD_2Cl_4, 90 °C) spectrum of this iPH further showed the absence of resonances for vinyl end-groups that might arise through chain termination via β-hydrogen transfer processes. Finally, a $^{13}C\{^1H\}$ NMR (200 MHz) stereochemical microstructure analysis of this same sample confirmed that chain growth propagation had occurred in a strict stereoselective and 1,2-regiospecific manner. Collectively, these results provide overwhelming evidence for quantitative formation of the desired Hf-based CPAM^{CF3} initiator from **4** and its ability to effect the stereospecific and regiospecific LCP of 1-hexene. Most importantly, however, a kinetic analysis not only established the expected linear relationship between M_n and time, but also that the observed R_p for this 1-hexene polymerization using the CPAM^{CF3} preinitiator **4** was six-times larger than that obtained using the corresponding CPAM^{CH3} preinitiator **2**. Finally, the LCP of propene using **4** was also conducted, and under our standard conditions, a more than eight-fold increase in the observed rate of polymerization could now be realized [*cf.* iPP from **2**: M_n = 6.2 kDa ($Đ$ = 1.63) vs from **4**: M_n = 49.9 kDa ($Đ$ = 1.62)].[6] Importantly, this higher R_p value for the Hf-based CPAM^{CF3} system based on **4** is achieved without a sacrifice in either the degree of stereo- or regioselectivity previously provided by **2**, and on a practical level, this means that the former can now be used to access a higher targeted molecular weight for the polyolefin product

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within a more reasonable polymerization time than that previously possible with the latter.

Although the exact origin of the electronic effects introduced by the α,α,α-trifluoroacetamidinate ligand into the CPAM family of initiators for the LCP and LCCTP of olefins still remains to be more firmly established through additional experimental studies and computational modeling, it is clear that these can operate in a synergistic fashion with previously established substituent-based steric effects. Efforts are now in progress to further develop the CPAM^{CF3} ligand set for both living and nonliving olefin polymerization catalysts.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00839.

Experimental details, supporting figures (PDF)

Accession Codes

CCDC 1869268−1869270 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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(6) Although no chain termination is evident for the LCP of either olefin by Hf-based CPAM initiators, a larger molecular weight distribution is observed for iPP relative to iPH (*cf.* $Đ$ (=M_w/M_n) of 1.62 vs 1.02, respectively). The origin of this difference is currently under investigation.

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(9) According to the mechanism of Scheme 1,

$$R_p = k_p\left[\frac{K_m[M]}{1 + K_m[M]}\right][A^n]$$

where M is monomer and A^n is propagator.

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(16) Details are provided in the Supporting Information.

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