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Communication

Migratory Insertion into a Hafnium−Phenyl Bond and a Ligand-Assisted Mechanism for Reversible Chain Transfer in the Living Coordinative Polymerization of Olefins

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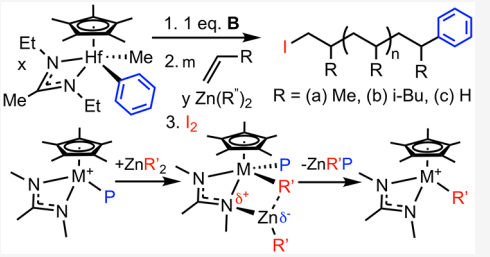
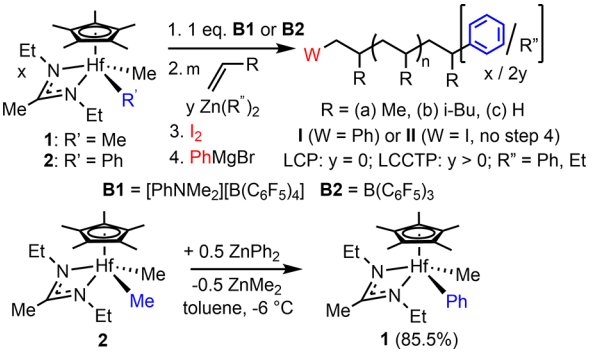
ABSTRACT: Results of a combined experimental and computational investigation are presented that (1) document phenyl group exchange and migratory insertion (MI) within neutral and cationic CPAM hafnium complexes bearing a Hf−Ph bond that are relevant to the living coordinative (chain transfer) polymerization of olefins to produce phenyl-terminated polyolefins, (2) establish that $\Delta G^{\ddagger}$ (initiation) < $\Delta G^{\ddagger}$ (propagation) for initial and subsequent MIs of ethene into a Hf−Ph bond of an ion pair initiator for living coordinative polymerization, and (3) support an alternative stepwise, ligand-assisted mechanism for reversible chain transfer that resolves problematic issues with the often-invoked direct chain exchange process proceeding through a four-membered-ring bis(μ-bridging chain) intermediate.



In response to the global plastic waste crisis, there is an immediate and critical need for new commercially viable polyolefin materials that can be readily produced from the same small set of industrially relevant olefin monomers, but that are more amenable to safe environmental degradation and energy efficient thermal, photolytic, and chemical recycle or upcycle.[1−3] Over the past two decades we have made advances with the development of (stereoselective) two-, three-, and multi-state living coordinative polymerization (LCP) and living coordinative chain transfer polymerization (LCCTP) of a wide variety of α-olefins and α,ω-nonconjugated dienes that now provide a versatile toolbox of methods for systematically exploring multi-dimensional structure/property relationships of an almost unlimited spectrum of existing, fundamentally new, and yet-to-be-conceived classes of polyolefin materials.[4] Recently, we reported a highly versatile, new synthetic process for the scalable production of practical quantities of α,ω-difunctionalized homo- and heterotelechelic polyolefins, **I** and **II**, respectively, that is based on the (stereoselective) LCCTP of α-olefins using diphenylzinc ($ZnPh_2$) as a chain transfer agent (CTA: $y > 0$) in combination with a member of the family of cyclopentadienyl amidinate (CPAM) group 4 metal complexes serving as a pre-initiator that is "activated" by a stoichiometric amount of a borate or borane co-initiator (**B**) according to Scheme 1.[5] The phenyl end-groups of **I** and **II** then serve as synthons for a range of different end-group functionalities that can be "unmasked" through a variety of simple post-polymerization processes that proceed in near quantitative fashion, such as aromatic electrophilic substitution. This new library of accessible telechelic polyolefins can now be used for the design of higher molar mass materials that incorporate "weak chemical links" for efficient chemical recycle, as well as di-, tri-, and multi-block co-polymers that can function, for example, as blend compatibilizers for two or more plastic waste streams (e.g., polyolefins and polyesters).[2,3]

Scheme 1. Phenyl and Polymeryl Group Transfers between $ZnPh_2$ and CPAM Group 4 Metal Ion Pair and Neutral Complexes



The effectiveness of $ZnPh_2$ as a CTA in the LCCTP process at the top of Scheme 1 was unexpected and very surprising given the prior reports by Gibson and co-workers[6] and Tonks and co-workers[7] which not only showed its inability to serve as a CTA in their respective non-living CCTP systems, but also

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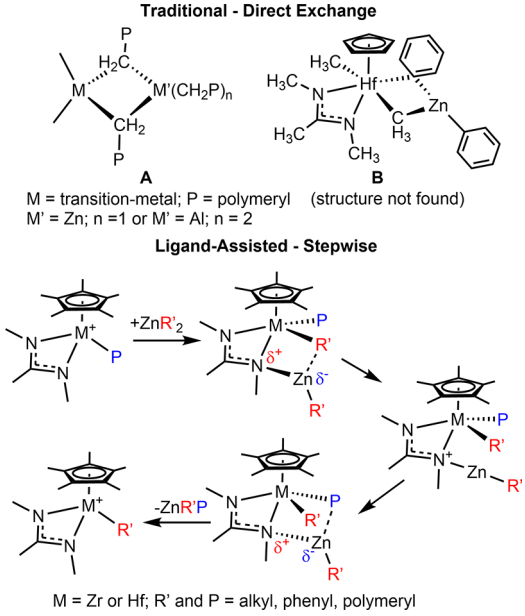
proposed (by the latter group) that it had a deleterious impact on catalyst activity by engaging in irreversible phenylation of the active species. This conclusion raised the question in our minds as to what precedent exists for migratory insertion (MI) of an olefin into a metal−phenyl bond of a transition-metal complex that is relevant to coordination polymerization—and surprisingly, to the best of our knowledge, the answer is none. To be sure, due to the seminal contributions of Jordan and co-workers[8] and others,[9] well-characterized $[Cp_2M\text{-}Ph]^+$ (M = Zr and Hf) complexes have been known for a long time, but only the outcome of single insertion of acetonitrile and alkynes into the M−Ph bond of these species were reported. Importantly, in the Jordan's group work, an attempt to polymerize ethene with their complexes failed. Naturally, this gap in fundamental knowledge then led us to question what makes our CPAM initiator system for LCCTP so effective with not only $ZnPh_2$, but with other ZnR_2 and AlR_3 CTAs as well.[4,5] Herein, we now report the results of a combined experimental and computational investigation that was undertaken to shed new light on an answer to this question, as well as to document the ability of a CPAM derivative possessing a metal−phenyl bond to function as a pre-initiator for both the LCP and LCCTP of olefins. As will be revealed, both goals were achieved, and in fact, the results of this study provide strong support for an alternative mechanism for group and polymeryl (chain) transfers that circumvents several problematic issues associated with the traditional mechanism that is often invoked. More to the point, as Scheme 2 presents, chain transfer between a transition-metal propagator and a population of CTA species is almost invariably depicted as occurring via a direct exchange process involving a proposed bimetallic four-membered ring intermediate **A** with two μ-bridging chain interactions.[6,7,10,11] To the best of our knowledge, however, there is actually no experimental evidence or computational support for such a species as **A** in any reports of living and non-living CCTP.[12] We are further skeptical of how **A** can accommodate the substantial increase in non-bonded steric interactions that must arise as three and possibly four (depending on whether ZnR_2 or AlR_3 is used as CTA) sterically encumbered growing polymer chains are brought together in close proximity through formation of two μ-bridging bonding interactions. Indeed, as will be revealed, our failure to computationally locate the traditionally expected structure **B** for phenyl group exchange led instead to discovery of the foundations of an alternative stepwise ligand-assisted mechanism for group and chain transfer that is shown in Scheme 2. Importantly, this new mechanism not only reduces the steric penalty for chain exchange, but it also provides a rational electronic basis for how the energy barrier for group exchange can be reduced. Finally, a survey of the literature for transition-metal complexes that are known to be effective in the CCTP of olefins suggests that this ligand-assisted mechanism may well be a general one.

Scheme 2. Proposed Traditional (Top) vs Ligand-Assisted (Bottom) Mechanisms for Reversible Group and Polymeryl (Chain) Transfers



As Scheme 1 presents, the desired new target, $\{(\eta^5\text{-}C_5Me_5)[\kappa^2\text{-}N(Et)C(Me)N(Et)]\}Hf(Me)(Ph)$ (**1**), was easily prepared in one-step and in high yield from the exchange reaction between known $\{(\eta^5\text{-}C_5Me_5)[\kappa^2\text{-}N(Et)C(Me)N(Et)]\}Hf(Me)_2$ (**2**)[4d] and 0.5 equiv of $ZnPh_2$ in toluene at −6 °C.[13] Analytically pure **1** was obtained by recrystallization from a toluene/pentane solvent mixture at −30 °C, and characterization by ^1H and ^{13}C NMR spectroscopy and structural analysis of single crystals by X-ray crystallography is fully consistent with the structure of **1** that is depicted. Finally, ^1H NMR spectroscopy was used to determine that **1** is thermally unstable and decomposes in solution above 50 °C.

The ability of **1** to serve as a pre-initiator for LCP and LCCTP via insertion into the Hf−Ph bond was investigated according to the methods summarized in Scheme 1. Thus, to begin, activation of **1** was performed using 1.1 equiv of the borate co-initiator, $[PhNHMe_2][B(C_6F_5)_4]$ (**B1**), to generate the corresponding active ion pair initiator, which was then added to a propene-saturated toluene solution pre-cooled to −10 °C. After stirring under a positive pressure (5 psi) of propene for 30 min, LCP was quenched by the addition of excess I_2, and the product, α-iodo-ω-phenyl atactic polypropene, I-aPP-Ph (**IIa**), was isolated in high yield.[13] Size exclusion chromatography (SEC) analysis of **IIa**, using dual detectors [refractive index (RI) and ultraviolet (UV: λ = 264 nm)] provided a number-average molar mass index, M_n, and molar mass distribution (MMD) dispersity, $Đ$, of 17.7 kDa and 1.14, respectively. The monomodal nature of the MMD profile and very small $Đ$ value, coupled with evidence for a high degree of phenyl end-group termination in **IIa** as determined from an overlay of the RI and UV detector traces (see Figure S9), strongly suggests that activation of **1** by **B1** was highly chemoselective for generating the desired CPAM ion pair initiator. Further, this species then engaged in very efficient and rapid initiation through MI of propene into the Hf−Ph bond. A ^1H NMR spectrum of **IIa** also clearly reveals the expected resonances associated with both the α-iodo and the ω-phenyl end-groups (see Figure S3). For an investigation of LCCTP, **1** was again activated with **B1** and the active initiator added to a toluene solution of 238 equiv of 4-methyl-1-pentene as the olefin monomer and 5 equiv of $ZnEt_2$. Here, the choice of using $ZnEt_2$ rather than $ZnPh_2$ as the CTA is to have the ability to quantify the efficiency of Ph group transfer from the active initiator under LCCTP conditions. After an I_2 quench and the usual workup, an excellent yield of α-iodo, ω-(Ph/Et)-terminated atactic poly(4-methyl-1-pentene), I-aPMP-(Ph/Et) (**IIb**) was obtained.[13] In this case, **IIb** was

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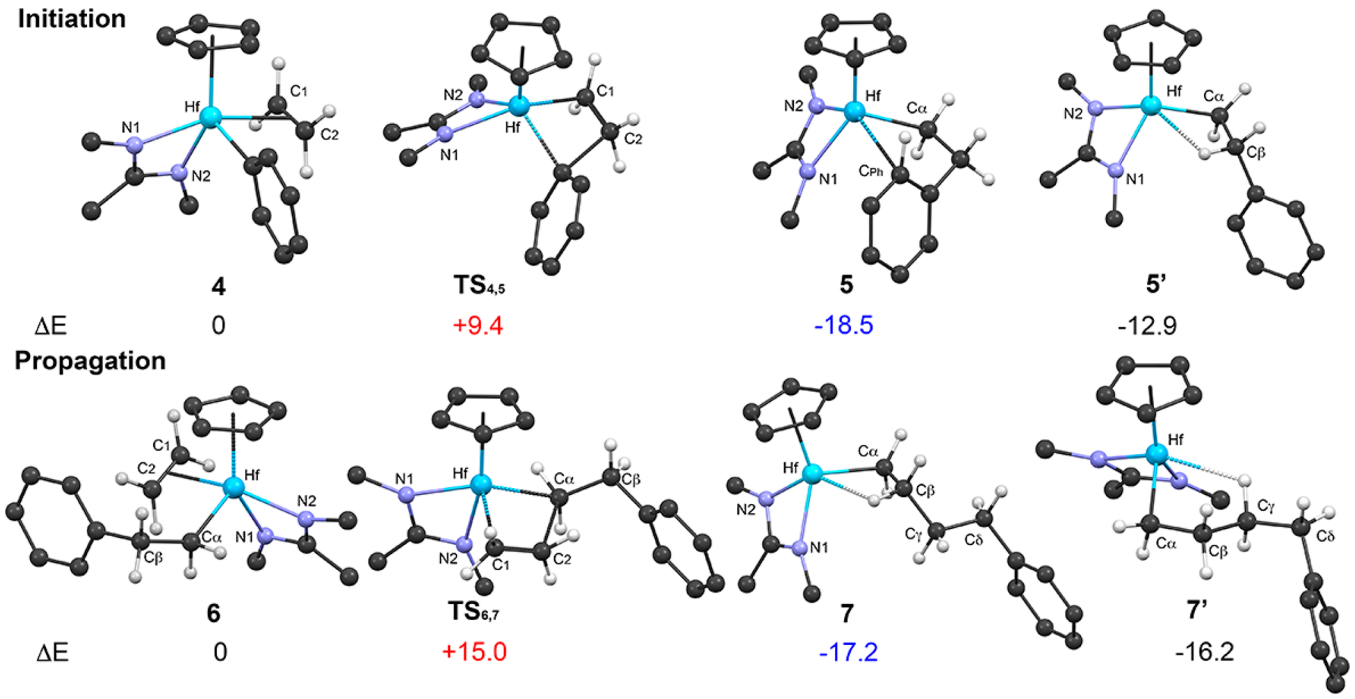

Figure 1. Comparison of computed (Gaussian 09, DFT (B3LYP/LANL2DZ (Hf, Zn)/6-31G**) structures and relative energies (kcal mol^{-1}) of reactant, transition state, and product for initiation and propagation in the LCP of ethene by **3** as initiator.

quantitatively converted into the corresponding α-iodo-ω-acetophenone-terminated heterotelechelic, I-aPMP-PhC(O)-Me (**IIIb**), through Friedel–Crafts acylation using excess equivalents of acetyl chloride (AcCl) and aluminum chloride ($AlCl_3$), according to our previously published procedure.[5b] Dual detection SEC analysis of **IIIb** once again confirmed a high degree of phenyl end-groups being present and provided M_n and $Đ$ values of 1.6 kDa and 1.4, respectively, that are fully consistent with highly efficient LCCTP (see Figure S11). Here, it is common to observe broader dispersity values at very low DP_n values where differences in the rates of initiation and chain transfer involving early populations of $ZnEt_2$ and ZnEt-(polymeryl) species exist.[14] Since the respective phenyl and acetophenone moieties of **IIb** and **IIIb** are diluted by ethyl end-groups in a theoretical 1:10 ratio, the ability to clearly observe all the expected end-group resonances in these telechelic polyolefins by ^{1}H NMR spectroscopy is an excellent testimonial to the ability of activated **1** to engage in productive MI and chain transfer involving the Hf–Ph bond (see Figure S6).[13] As a final preliminary study, the borane activator, $B(C_6F_5)_3$ (**B2**), was now employed with **1** for the LCP of ethene (5 psi) in chlorobenzene at 10 °C for 5 min, followed by an I_2 reactive quench to produce I-PE-Ph (**IIc**). Figures S8 and S9 present the ^{1}H and inverse-gated $^{13}C\{^1H\}$ NMR spectra for this material, and end-group analysis using these data establish that near quantitative chemoselective methyl group abstraction of **1** by **B2** occurred to provide **IIc** with a M_n value of 25.8 kDa.

A preliminary computational investigation of initiation and propagation events in the LCP of ethene by the active ion pair derived from **1** and **B1** was performed using the truncated ligand set, CPAM′ = (η^5-C_5H_5)[N(Me)C(Me)N(Me)], which was shown to provide a reasonable facsimile for the intermediates and transition states involved. All calculations were performed in the absence of solvent and borate counteranions.[15,16] Finally, all optimized structures corresponding to relevant potential energy surface (PES) minima and transition states are provided within a master CIF file as part of the Supporting Information (SI) that can be downloaded and interrogated for specific geometric parameters of interest.

Figure 1 presents the structures for [(CPAM′)Hf(Ph)(η^2-C_2H_4)] (**4**) and [(CPAM′)Hf(CH_2CH_2Ph)]$^+$ (**5**) that are relevant to initiation involving the first MI of ethene into the Hf–Ph bond of [(CPAM′)Hf(Ph)]$^+$ (**3**) (not shown; see SI) that proceeds through the transition state, $\mathbf{TS_{4,5}}$. The calculated activation energy barrier for this MI step is +9.4 kcal mol^{-1}. This value can be compared to the activation energy barrier of +15.0 kcal mol^{-1} that was determined for subsequent MI of ethene into the Hf–C_{alkyl} bond of [(CPAM′)Hf(CH_2CH_2Ph)(η^2-C_2H_4)]$^+$ (**6**) to provide [(CPAM′)Hf({CH_2CH_2}$_2$Ph)]$^+$ (**7**) for chain growth proceeding through $\mathbf{TS_{6,7}}$. These computational results are in keeping with the experimental observations of a narrow MMD and a small $Đ$ value for **IIa** that support the conclusion that initiation is fast relative to propagation. Finally, for some of the products of MI, more than one minimum was located corresponding to different agostic interactions between the alkyl substituent and the Hf center, but in no case was an exhaustive PES search performed to identify all possible minima. For example, Figure 1 shows that the 2-phenylethyl substituent of **5** can engage in a *C*-agostic interaction with the phenyl group as the lowest energy isomer that is favored by 5.6 kcal mol^{-1} over the corresponding isomer **5′** that features a stabilizing β-hydrogen agostic interaction. For the second and subsequent MIs of ethene, the lowest energy isomer of the product was now determined to be the one with an intramolecular β-hydrogen agostic interaction as shown in the structure of **7** and for [(CPAM′)Hf({CH_2CH_2}$_3$Ph)]$^+$ (**8**) (not shown; see SI). However, the γ-hydrogen agostic isomer for the former is only about 1 kcal mol^{-1} less stable as

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exemplified by the structure and energy reported for 7′ in Figure 1.

As presented in the introductory statements, we were also interested in computationally investigating the phenyl group exchange between $ZnPh_2$ and the neutral CPAM dimethyl complex **2**. After failing to find either a minimum or transition state corresponding to the 1:1 adduct with structure **B** (see Scheme 2), a wider PES search was conducted, and gratifyingly, this yielded the alternative 1:1 adduct structure of **9** as a minimum that is shown in Figure 2. Notable structural

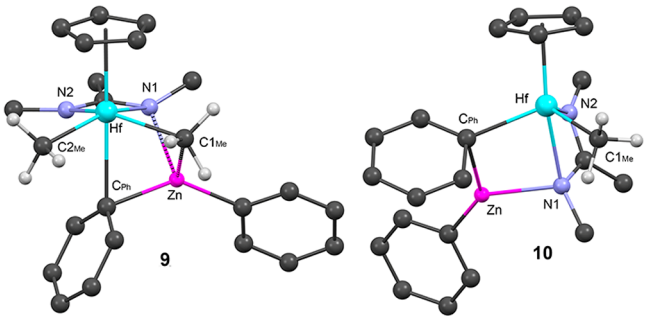

Figure 2. Computational optimized structures for the 1:1 adducts **9** and **10** which are PES minima.

features of **9** include a short distance between the Zn and one of the amidinate nitrogen atoms, d(Zn−N1) = 2.215 Å, that is associated with a longer Hf−N distance [cf. d(Hf−N1) = 2.517 Å vs d(Hf−N2) = 2.239 Å], and a μ-bridging phenyl group between Zn and Hf, with $d(Zn-C_{Ph})$ = 2.146 Å and $d(Hf-C_{Ph})$ = 2.619 Å. Finally, the carbon atom ($C1_{Me}$) of one of the Hf-bonded methyl groups is also in close proximity to the Zn center at $d(C1_{Me}-Zn)$ = 2.541 Å. These structural trends are also observed with contracted distances in the optimized PES minimum structure of the 1:1 adduct **10** that is formed between $ZnPh_2$ and the cationic complex **3**. More specifically, d(Zn−N1) = 2.184 Å, $d(Zn-C_{Ph})$ = 2.289 Å, $d(Hf-C_{Ph})$ = 2.313 Å, d(Hf−N1) = 2.420 Å, d(Hf−N2) = 2.206, and $d(Hf-C_{Me})$ = 2.239 Å.

The structural features observed for both **9** and **10** provide support for the proposed stepwise ligand-assisted group and chain transfer mechanism for LCCTP that is presented in Scheme 2. To begin, initial coordination of $ZnPh_2$ to one of the amidinate nitrogen atoms serves to generate partial positive charge on this nitrogen and partial negative charge on zinc as shown. These partial charges, in turn, increase the electrophilicity of the Hf center, while also enhancing the nucleophilicity of the transferring group to promote transfer through a bridging interaction. Complete transfer of the group from Zn to Hf now occurs to place the full positive charge on nitrogen. Finally, reversal of this sequence of steps provides the pathway for completion of the exchange process. As noted, this stepwise ligand-assisted chain transfer mechanism solves both the steric problem of bringing two or more polymeryl chains together at the same time, while also providing a lower energy barrier for exchange where the nitrogen atom can be viewed as a variable reservoir of electron density.

In conclusion, the present report establishes both experimentally and computationally that there is no fundamental restriction for MI of olefins into an early-transition-metal−phenyl bond, and in fact, one might wish to now incorporate this structural feature as a key design element for next generation initiators for LCP. In this regard, the incorporation of nitrogen-rich ligands that can participate as a key facilitating element in the proposed stepwise ligand-assisted chain transfer process might also lead to more versatile LCCTP systems. Here it is perhaps not coincidental to find that the bis(imino)pyridine iron complexes originally reported by Gibson and co-workers[6] for efficient CCTP of ethene, the hafnium pyridyl-amido complexes reported by Arriola and co-workers[10] for "chain-shuttling" co-polymerization of ethene and 1-octene, and the amidinate hafnium complexes of Kempe and co-workers[11a] for the CCTP of ethene all utilize either ZnR_2 and AlR_3 as CTAs and all are supported by nitrogen-rich ligands. Indeed, preliminary computational results reveal that a 1:1 complex between the Dow-related cationic Hf pyridyl-amido complex and $ZnPh_2$ also exists as a PES minimum with Zn−N and Hf−μPh−Zn bonding interactions similar to those of **10**. Additional efforts to extend the present findings and hypotheses are currently underway, the results of which will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.2c00364.

Experimental and computational details, including synthetic procedures and crystallographic analysis of **1** (PDF)

Computed structures of minima and transition states (CIF)

Accession Codes

CCDC 2191902 contains 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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