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Cyclopentadienyl Amidinate Ligand Directing Effects in the Enantioselective Living Coordinative Chain Transfer Polymerization of 1,5-Hexadiene

Cole M. Burrows, Peter Y. Zavalij and Lawrence R. Sita *

Department of Chemistry and Biochemistry, University of Maryland College Park, College Park, MD 20742, USA
* Correspondence: lsita@umd.edu

Abstract: The new chiral and configurationally stable cyclopentadienyl amidinate (CPAM) hafnium complexes, (R_C, R_{Hf})-**2** and (S_C, S_{Hf})-**3**, have been obtained in enantio- and diastereomerically pure form. Upon activation with the borate co-initiator, [$PhNHMe_2$][$B(C_6F_5)_4$] (**B1**), **2** and **3** can serve as pre-initiators for the enantioselective living coordinative polymerization (LCP) and living coordinative chain transfer polymerization (LCCTP) of 1,5-hexadiene to provide optically active poly (methylene-1,3-cyclopentane) (PMCP) and end-group-functionalized PMCP (x-PMCP) in scalable quantities, respectively. ^{13}C NMR stereochemical microstructural analyses reveal the role of ligand directing effects for the two-step propagation mechanism of 1,2-migratory insertion/ring-closing cyclization and structure/property relationships for these new PMCP and x-PMCP materials.

Keywords: living; chain transfer; polymerization; nonconjugated dienes; chiral liquid crystal

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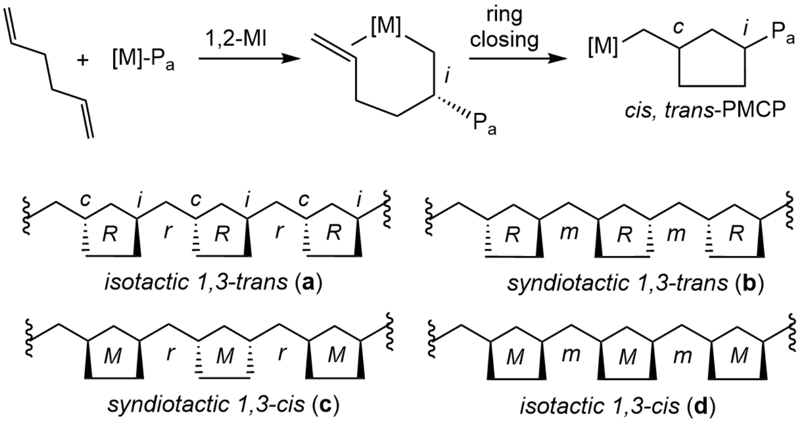
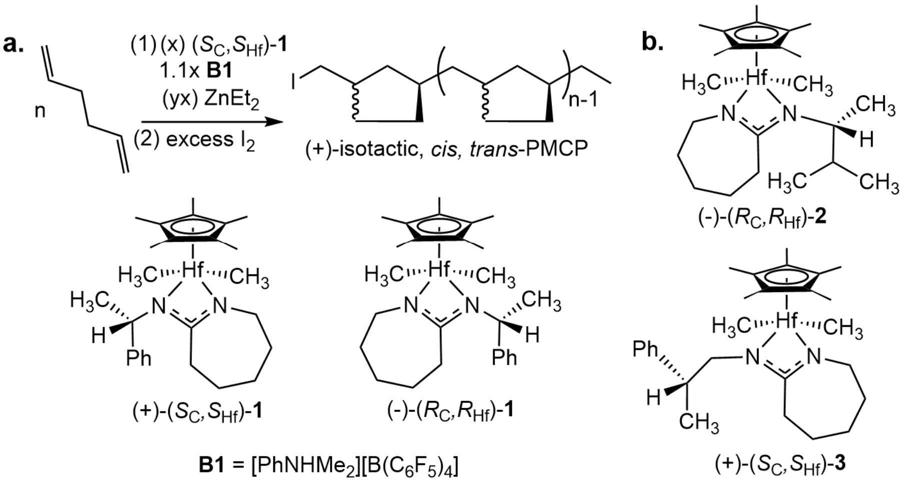
1. Introduction

The transition metal-mediated coordination polymerization of abundant and industrially significant olefin monomers, such as ethylene and propylene, remains a powerful tool that can be used to discover, design, and commercialize new polyolefin materials that are both of scientific interest and of technological benefit to society [1–5]. Within this scope, the coordination polymerization of 1,5-hexadiene has long been of interest due to a two-step mode of propagation involving initial 1,2-migratory insertion (1,2-MI) of one unsaturated end of the monomer, followed by cyclization insertion of the other unsaturated end to provide a poly(methylene-1,3-cyclopentane) (PMCP) product according to Scheme 1 [6–21]. It is well known that the supporting ligand environment about the transition metal centers of the propagating species dictates the degree of stereoregularity for both the 1,2-MI step and the *cis*/*trans* ratio of the 1,3-cyclopentane fragment of the repeat unit. As further revealed by the four limiting forms, **a**–**d**, in Scheme 1, the stereochemical microstructure (also known as tacticity) of PMCP is much more complex than that of polyolefins derived from α-olefins, which can be described as having atactic, isotactic, or syndiotactic limiting forms [22]. Designating the relative configurations of adjacent stereocenters within and between 1,3-cyclopentane units of PMCP as *meso* (*m*) and racemic (*r*) for the former and as *M* and *R* for the latter allows one to uniquely classify the symmetry characteristics of different 'grades' that can then correlate with physical properties. Thus, in the case of the isotactic, *trans* form **a** with *RrR* dyads, the absence of mirror planes perpendicular to the extended chain establishes it as being chiral and, accordingly, with the ability to manifest optical activity. On the other hand, the isotactic, *cis* form **d** with *MmM* dyads is achiral and devoid of optical activity even if propagation proceeds in a stereospecific manner. In practice, if there is a sufficient level of *trans* 1,3-cyclopentane formation during enantioselective coordinative cyclopolymerization of 1,5-hexadiene using homochiral catalysts, the resulting PMCP product will display some degree of optical activity [16–21]. The rigid-rod nature of the conformationally restricted polymer backbone of PMCP also serves to confer crystallinity and liquid crystal properties [20,21]. The latter is of interest for the design and development of new self-assembling photonic soft materials if practical and scalable quantities of optically active, end-group-functionalized PMCP materials (x-PMCP) can be made available. Surprisingly, there has only been one report in the literature regarding the production of an achiral x-PMCP material (x = –OH) that was used as a building block for a more advanced material [23,24]. Recently, we reported that the homochiral and configurationally stable cyclopentadienyl amidinate (CPAM) hafnium complexes, (+)-(S_C, S_{Hf})-**1** and (−)-(R_C, R_{Hf})-**1**, can serve as effective pre-initiators for the enantioselective living coordinative polymerization (LCP) and living coordinative chain transfer polymerization (LCCTP) of 1,5-hexadiene to provide desired quantities of optically active (+)- or (−)- end-group-functionalized PMCP according to Scheme 2 [25–32]. In the present report, we present the results of an investigation to determine the impact that changes in the non-bonded steric environment of the supporting amidinate fragment can have on the stereochemical microstructure and associated properties of x-PMCP materials through synthesis and evaluation of the new optically active and configurationally stable CPAM group 4 metal complexes **2** and **3** shown in Scheme 2.



Scheme 1. (**top**) Two-step propagation of coordination polymerization of 1,5-hexadiene to produce PMCP; (**bottom**) four limiting stereochemical forms for *cis* and *trans* PMCP.

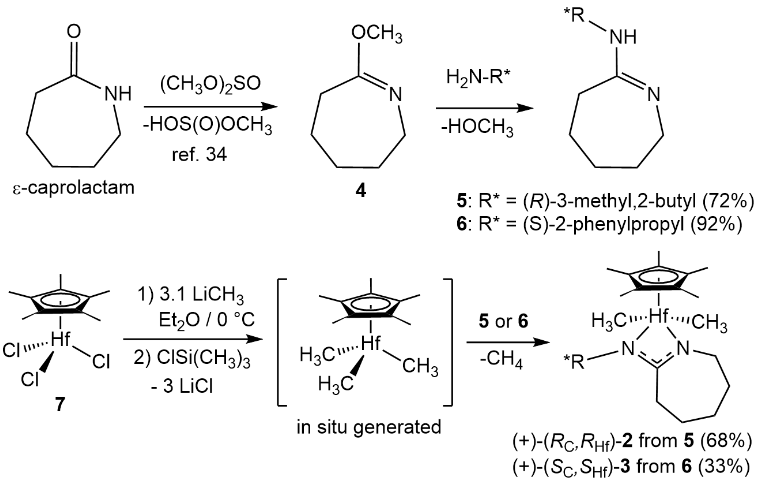


Scheme 2. (**a**) LCCTP of 1,5-hexadiene with (+)-**1** using $ZnEt_2$ as chain transfer agent and a reactive I_2 quench to provide (+)-I-PMCP; (**b**) structures of new CPAM pre-initiators investigated in the present report.

2. Results and Discussion

2.1. Synthesis of New CPAM Hafnuium Pre-Initiators **2** and **3**

Scheme 3 presents the synthetic methods that were used to obtain the new CPAM hafnium complexes, **2** and **3**, in a manner analogous to those used to produce **1** [25,26,33]. To begin, the O-Me lactim intermediate **4** was obtained from ε-caprolactam by the procedure originally reported by Benson and Carins [34,35]. Subsequent condensation of **4** with commercially available (−)-(*R*)-2-amino-3-methylbutane and (+)-(*S*)-β-methylphenethylamine provided the new homochiral caproamidines, **5** and **6**, respectively, in excellent isolated yields. The desired CPAM hafnium derivatives, **2** and **3**, were then obtained in moderate yields by protolytic addition of the caproamidines to Cp*HfMe$_3$ (**7**) that was generated in situ from commercially available Cp*HfCl$_3$ (**8**) and a slight stoichiometric excess (3.1 equivalents) of methyllithium according to Scheme 3. As noted, we have found that higher yields can be achieved by the addition of chlorotrimethylsilane (ClSiMe$_3$) after the methylation step, which serves to quench any basic impurities that can catalyze decomposition of **7** prior to the addition of the amidine. Characterization of the new crystalline CPAM hafnium complexes, **2** and **3**, by ^{1}H and ^{13}C NMR (400 and 100 MHz, respectively, toluene-d$_8$) spectroscopy provided spectra consistent with the structures depicted in Scheme 2b. Most notably, observation of only a single set of two resonances for the diastereotopic methyl groups bonded to Hf provided strong evidence that a single diastereomer had been produced in each case (see Figures S5 and S7 in Supporting Information). This conclusion was further supported by conducting variable temperature ^{1}H NMR spectroscopy between the temperatures of 25 °C and 90 °C that revealed the barriers to 'amidinate-ring-flipping' epimerization of the transition metal center to be sufficiently high enough to confer configurational stability of **2** and **3**.



Scheme 3. Synthesis of homochiral amidines, **5** and **6**, and the CPAM hafnium complexes, **2** and **3**.

2.2. Structural Characterization of **2** and **3**

Single crystals of **2** were obtained by crystallization from a mixed hydrocarbon (toluene/pentane) solution at a low temperature of −30 °C. Figure 1 provides geometric parameters for the solid-state molecular structure of **2** as obtained through single crystal X-ray analysis. As expected, only a single diastereomer is observed within the unit cell, and based on standard convention for assigning the absolute configuration of chiral piano-stool metal complexes, the structure shown in Figure 1 is for (R_C, R_{Hf})-**2**, which is in keeping with the previously reported (R_C, R_{Hf})-**1** diastereomer [36–40]. There is an asymmetry in the two Hf-N bond distances [cf. Hf1-N1 2.226(3) Å and Hf1-N2 2.257(3)] and a large difference in the sum of the bond angles around each nitrogen atom [cf. 355.34° for N1 and 358.60° for N2], which suggests that N2 has a weaker, dative bonding interaction and N1 has a stronger covalent bonding interaction with the hafnium metal center. The larger Hf1-N2-C21 bond angle of 142.5(2)° vis-à-vis the Hf1-N1-C14 bond angle of 138.6(2)°

also suggests that more steric congestion due to non-bonded steric interactions with the C11 methyl group exists relative to the more sterically open side of the C12 methyl group position. Finally, it is interesting to note that the C23-C24-C25 'isopropyl' fragment of the N-(*R*)-3-methyl-2-butyl substituent is located in a similar spatial position as the phenyl group of the N-(*R*)-1-phenylethyl substituent of (R_C, R_{Hf})-**1**, and this suggests that the Ph to isopropyl group replacement has caused little steric disruption in the overall favored geometry in going from **1** to **2**.

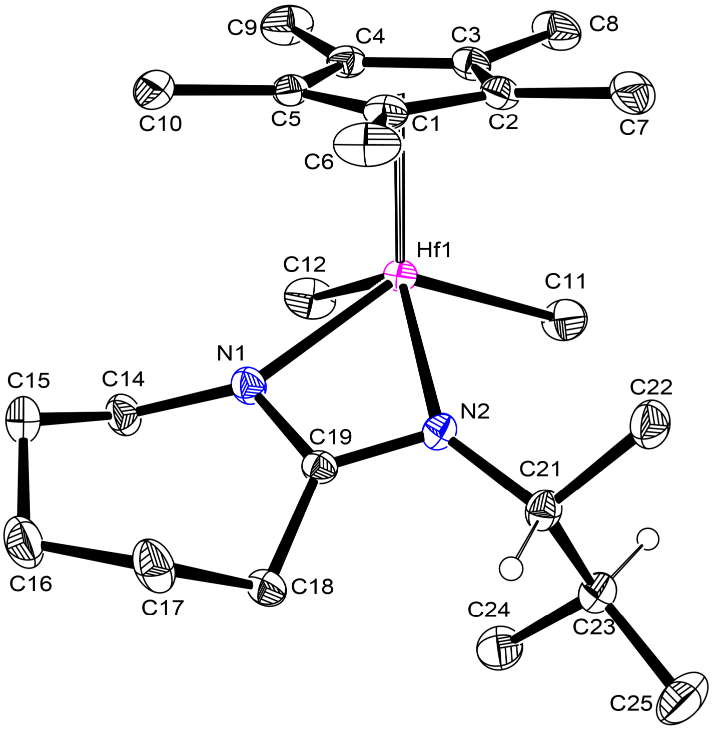


Figure 1. Molecular structure (30% thermal ellipsoids) of (R_C, R_{Hf})-**2**. Hydrogen atoms have been removed for the sake of clarity, except those on C21 and C23, which are represented by spheres of arbitrary size. Selected bond lengths (Å): Hf1-C11 2.244(4), Hf1-C12 2.234(3), Hf1-N1 2.226(3), Hf1-N2 2.257(3), C19-N1 1.325(4), C19-N2 1.333(4), N1-C14 1.465(4), and N2-C21 1.468(4). Selected bond angles (°): C11-Hf1-C12 87.70(16), N1-Hf1-N2 58.79(10), N1-C19-N2 111.7(3), Hf1-N1-C14 138.6(2), Hf1-N1-C19 95.24(19), C14-N1-C19 121.5(3), Hf1-N2-C21 142.5(2), Hf1-N2-C19 93.60(18), and C19-N2-C21 122.5(3).

Single crystals of **3** were also obtained and subjected to similar X-ray crystallographic analysis to provide the solid-state molecular structure that is presented in Figure 2. The selected bond distances and bond angles revealed for the single diastereomer found for the unit cell, (S_C, S_{Hf})-**3**, suggest that a decrease in non-bonded steric interactions involving the *N*-substituents, vis-à-vis those of (R_C, R_{Hf})-**2**, has occurred. Most notably, the sum of the bond angles indicates that N2 is closer to trigonal coplanarity, and the Hf1-N2-C21 bond angle of 140.0° is more acute in (S_C, S_{Hf})-**3** than the corresponding geometric parameters of those present in (R_C, R_{Hf})-**2**.

*2.3. Living Coordinative (Chain Transfer) Polymerization of 1,5-Hexadiene by (R_C, R_{Hf})-**2** and (S_C, S_{Hf})-**3** as Pre-Initiators*

To test the viability of the new homochiral and configurationally stable CPAM hafnium complexes **2** and **3** as pre-initiators, the living coordination polymerization (LCP) of 1,5-hexadiene was first carried out using the anilinium borate, $[PhNHMe_2][B(C_6F_5)_4]$ (**B1**), as the activating co-initiator according to our well-established procedures (see details in the Supporting Information) [6–8]. Gratifyingly, both complexes proved to be capable of generating active initiators that provided a good yield of semicrystalline PMCP product in each case (runs 1 and 2). The LCCTP of 1,5-hexadiene was next performed using the same initiating system that now included five equivalents of diethylzinc ($ZnEt_2$) as chain transfer agent (CTA). After the usual time for polymerization, LCCTP was quenched by the addition of excess equivalents of molecular iodine (I_2) to produce α-iodo-terminated PMCP products with lower expected molar mass.

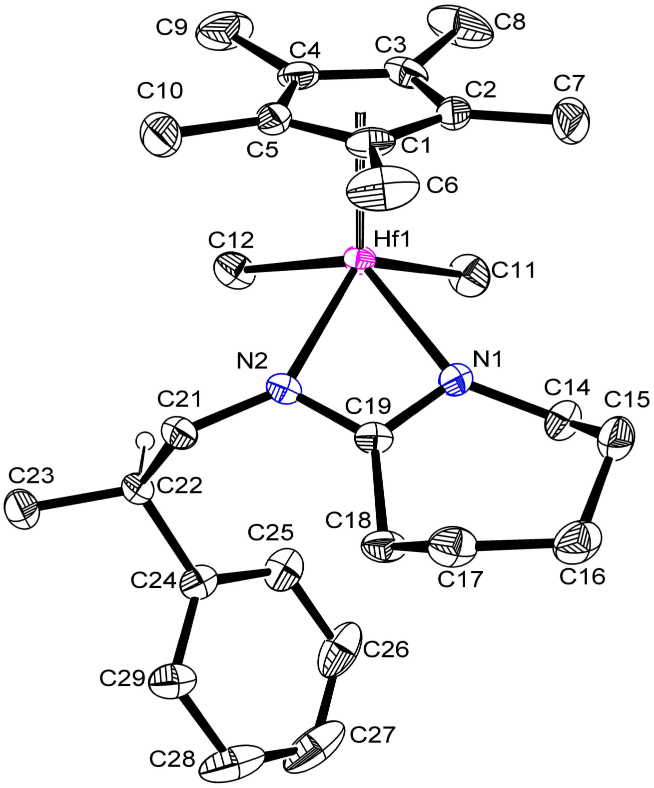


Figure 2. Molecular structure (30% thermal ellipsoids) of (S_C, S_{Hf})-**3**. Hydrogen atoms have been removed for the sake of clarity, except for C22, which is represented by a sphere of arbitrary size. Selected bond lengths (Å): Hf1-C11 2.239(3), Hf1-C12 2.251(3), Hf1-N1 2.230(3), Hf1-N2 2.231(2), C19-N1 1.329(4), C19-N2 1.331(4), N1-C14 1.459(4), and N2-C21 1.450(4). Selected bond angles (°): C11-Hf1-C12 90.51(15), N1-Hf1-N2 58.86(9), N1-C19-N2 111.0(3), Hf1-N1-C14 141.1(2), Hf1-N1-C19 94.91(19), C14-N1-C19 121.8(3), Hf1-N2-C21 140.0.(2), Hf1-N2-C19 94.81(18), and C19-N2-C21 124.5(3).

Table 1 presents details of the characterization data for all the new PMCP materials as obtained by ^1H and ^{13}C NMR (800 and 200 MHz, respectively, 1,1,2,2-tetrachloroethane-d_2, 110 °C) spectroscopy for microstructural information, gel permeation chromatography (GPC) for determination of molar mass indices and dispersity, and differential scanning calorimetry (DSC) for glass transition and melt transition temperatures, T_g and T_m, respectively. These data are consistent with the living character of coordination polymerizations conducted using CPAM complexes as pre-initiators in both the absence and presence of chain transfer agents [25–32]. We have also observed larger dispersity values when employing enantiopure and configurationally stable CPAM initiators, which we believe is the manifestation of a reversible equilibrium involving uncomplexed and complexed propagators due to increased steric interactions about the metal center by the bulky chiral *N*-substituent. ^1H NMR spectra are consistent with that expected for PMCP, and these reveal the presence of a small amount (e.g., 0.5% to 1%) of pendant ω-butenyl side chains that originate from failure of the monomer to cyclize following initial 1,2-MI (see Figure 1). Figure 3 presents the partial ^{13}C NMR spectra for the PMCP samples in which differences in the stereochemical microstructures are clearly evident. The most notable difference is the large increase in the formation of *trans*-1,3-cyclopentane units for the ring-closing step of propagation in PMCP obtained from (R_C, R_{Hf})-**2** vs. (S_C, S_{Hf})-**3** (cf. 70.4% vs. 41.1%, respectively) [6–31]. A more thorough investigation of differences in the stereochemical microstructure arising from differences in the degree of stereoregularity for the 1,2-MI step has not been performed. In keeping with prior observations by us and others, PMCP with a number-average molar mass index, $M_n \geq 10$ kDa, has a melting temperature, T_m, of between 70 °C and 100 °C, and with $M_n < 3$ kD, this phase transition is not always observed (cf. runs 3 and 4). Finally, it is of interest that the specific rotation, $[\alpha]_D$, values obtained for toluene solutions of the PMCP products are concentration dependent (see the last column of Table 1). In unpublished studies, we have obtained results showing that optically active *N*-PMCP substituents of perylene bisimide (PBI)-PMCP conjugates can direct the formation of chiral helical stacking of the perylene cores within chloroform solutions in a temperature- and concentration-dependent manner. It is very likely that the present observation of variances in optical rotation as a function of concentration is due to the liquid crystal nature of the rigid-rod PMCP polymer chains.

Table 1. Results of LCP and LCCTP of 1,5-hexadiene using (R_C, R_{Hf})-**2** and (S_C, S_{Hf})-**3** [a].

Run	Pre-Init.	$ZnEt_2$ (eq)	Yield (g)	M_n (kDa) [b]	*Đ* [b]	%*trans* [c]	T_g [d]	T_m [d]	$[\alpha]_D$ [e] (°)
1	(R_C, R_{Hf})-**2**	0	0.49	9.23	1.44	70.4	−4.77	78.0	−5.8/8.5
2	(S_C, S_{Hf})-**3**	0	0.51	24.2	1.36	41.1	2.95	94.8	3.2/−11.7
3	(R_C, R_{Hf})-**2**	5	0.85	1.44	1.18	72.7	n.o. [f]	n.o.	7.2/−3.4
4	(S_C, S_{Hf})-**3**	5	0.59	2.73	1.18	41.7	n.o.	n.o.	2.6/−9.9

[a] See SI for experimental details. [b] Determined by GPC. [c] Determined by NMR. [d] Determined by DSC. [e] c = 0.2/1.0 (mg mL^{-1}) in toluene. [f] Not observed.

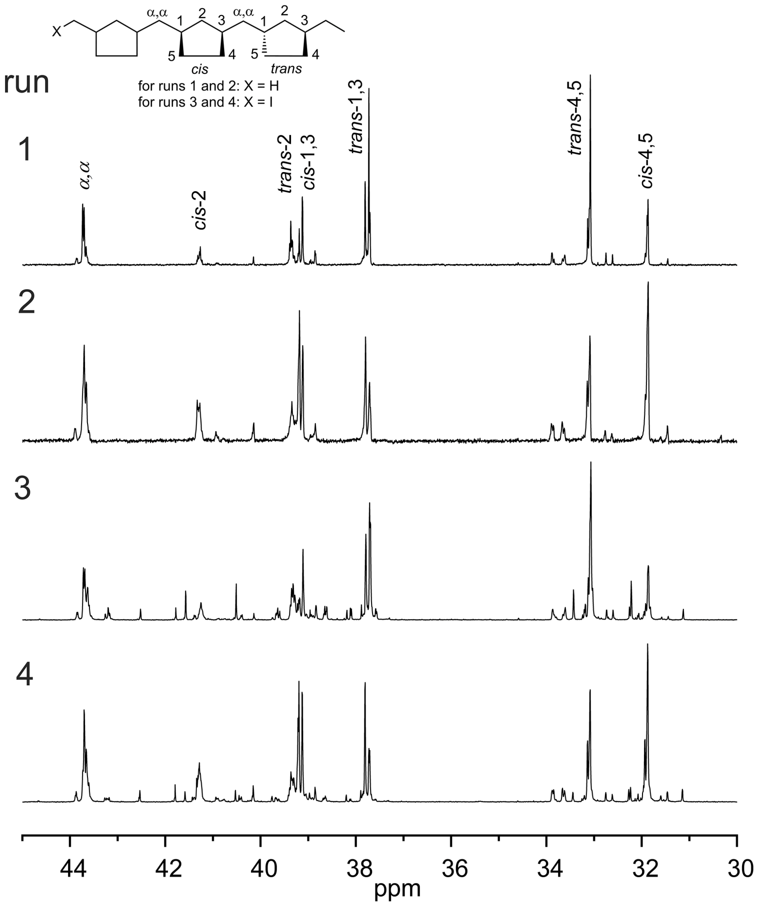


Figure 3. $^{13}C\{^1H\}$ NMR (200 MHz, 1,1,2,2-TCE-d_2, 100 °C) spectra for PMCP materials obtained from LCP (runs 1 and 2 of Table 1) with proton quench and LCCTP (runs 3 and 4 of Table 1) with I_2 quench of 1,5-hexadiene.

3. Conclusions

The present results serve to show that the unique configurational stability conferred to the transition metal by the bicyclic nature of caproamidinate coordination can be used to create a larger family of homochiral and diastereomerically pure CPAM hafnium complexes that can be used as pre-initiators for the enantioselective LCP and LCCTP of 1,5-hexadiene. Differences in the non-bonded steric interactions of the chiral alicyclic N-alkyl substituent can be used to manipulate the PMCP stereochemical microstructure, with the highest % *trans* value now being obtained for (R_C, R_{Hf})-**2**. Additional computational and experimental investigations are now in progress to identify new homochiral CPAM hafnium pre-initiator designs that might provide access to even higher % *trans* stereoregularity for end-group-functionalized PMCP building blocks possessing a maximum degree of chirality and optical activity as building blocks to advanced materials.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal14120944/s1.

Author Contributions: C.M.B. and L.R.S. shared in conceptualization of the research performed and analysis of the materials and conclusions reached. C.M.B. performed experimental work and L.R.S. provided supervision. P.Y.Z. performed crystallographic analyses. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: CCDC 2402541 and 2402542 contain the supplementary crystallographic data for (R_C, R_{Hf})-**2** and (S_C, S_{Hf})-**3**, respectively. 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.

Conflicts of Interest: The corresponding author has a financial interest in the university spin-out company, Precision Polyolefins, LLC (PPL). This work did not involve any PPL personnel, funding, or other resources, and all new intellectual property has been disclosed in accordance with state and federal requirements.

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