New Insights into the Polymerization of Methyl Methacrylate Initiated by Rare-Earth Borohydride Complexes: A Combined Experimental and Computational Approach

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Abstract: Polymerization of methyl methacrylate (MMA) initiated by the rare-earth borohydride complexes [Ln-$(BH_4)_3(thf)_3$] (Ln=Nd, Sm) or [Sm-$(BH_4)(Cp*)_2(thf)$] (Cp*=η-C_5Me_5) proceeds at ambient temperature to give rather syndiotactic poly(methyl methacrylate) (PMMA) with molar masses $\bar{M}_n$ higher than expected and quite broad molar mass distributions, which is consistent with a poor initiation efficiency. The polymerization of MMA was investigated by performing density functional theory (DFT) calculations on an η-C_5H_5 model metallocene and showed that in the reaction of [Eu$(BH_4)(Cp)_2$] with MMA the borate [Eu$(Cp)_2${$(OBH_3)(OMe)C=C(Me)_2$}] (**e-2**) complex, which forms via the enolate [Eu$(Cp)_2${$O(OMe)C=C(Me)_2$}] (**e**), is calculated to be exer-

gonic and is the most likely of all of the possible products. This product is favored because the reaction that leads to the formation of carboxylate [Eu$(Cp)_2${$OOC-C(Me)(=CH_2)$}] (**f**) is thermodynamically favorable, but kinetically disfavored, and both of the potential products from a Markovnikov [Eu$(Cp)_2${$O(OMe)C-CH(Me)-(CH_2BH_3)$}] (**g**) or anti-Markovnikov [Eu$(Cp)_2${$O(OMe)C-C(Me_2)(BH_3)$}] (**h**) hydroboration reaction are also kinetically inaccessible. Similar computational results were obtained for the reaction of [Eu$(BH_4)_3$] and MMA with

all of the products showing extra stabilization. The DFT calculations performed by using [Eu$(Cp)_2(H)$] to model the mechanism previously reported for the polymerization of MMA initiated by [Sm$(Cp*)_2(H)$]$_2$ confirmed the favorable exergonic formation of the intermediate [Eu$(Cp)_2${$O(OMe)C=C(Me)_2$}] (**e''**) as the kinetic product, this enolate species ultimately leads to the formation of PMMA as experimentally observed. Replacing H by BH_4 thus prevents the 1,4-addition of the [Eu$(BH_4)(Cp)_2$] borohydride ligand to the first incoming MMA molecule and instead favors the formation of the borate complex **e-2**. This intermediate is the somewhat active species in the polymerization of MMA initiated by the borohydride precursors [Ln$(BH_4)_3$-$(thf)_3$] or [Sm$(BH_4)(Cp*)_2(thf)$].

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Introduction

Over the past few decades, rare-earth complexes have received much interest as initiators for the living polymerization of polar monomers and many efficient systems have been unveiled. Group 3 organometallic compounds have been successfully applied to the anionic polymerization of alkyl acrylates.[1–4] The ligand array has been shown to significantly influence not only the structure of the initiator, but also its activity, efficiency, and selectivity in the polymerization process, as well as polymer features such as the molar mass, the molar mass distribution, the microstructure, and the stereoregularity.[5–7]

The most significant breakthrough has been achieved by Yasuda who successfully polymerized methyl methacrylate

(MMA) by using bis(pentamethylcyclopentadienyl)lanthanide hydride or the methyl complexes [Ln(Cp*)$_2$(R)] (Cp* = C$_5$Me$_5$; Ln = Sm, Yb, Y, Lu; R = H, Me).[2,8–12] Highly syndiotactic (>95% rr) polymers with high molar masses ($\bar{M}_n$ ≈ 10^6) and extremely narrow molar mass distributions ($\bar{M}_w$/$\bar{M}_n$ = 1.02–1.05) have been obtained with a quantitative conversion (>99%) in a short time. To date, fulfillment of the requirements for the living polymerization of MMA to give syndio-rich polymers remains unmatched.

The isospecific (94% mm) polymerization of MMA was accomplished by Marks and co-workers by using the chiral lanthanide metallocene amido complex [La{Me$_2$Si(C$_5$Me$_4$)-(C$_5$H$_3$-(1S),(2S),(5R)-neomenthyl)}(NSiMe$_3$)$_2$].[2,13] Following this pioneering work, Yasuda and co-workers prepared the most iso-rich (97% mm) PMMA from the homoleptic alkyl lanthanide complex [Yb{C(SiMe$_3$)$_3$}$_2$].[14] Other bis-initiators evaluated by Knjazhanski and co-workers, such as the divalent lanthanidocenes [Yb(SiMe$_3$L)$_2$(thf)] (L = indenyl, fluorenyl), have also afforded iso-rich PMMA.[15,16]

As shown by Novak and Bochmann and their co-workers, bimetallic complexes, such as the bis-allyl [{Sm(Cp*)$_2$(μ-η^3-CH$_2$CHCH-)}$_2$],[17] [(Sm{C$_5$H$_3$(SiMe$_3$)$_2$}$_3${μ-K(thf)$_2$})$_2$],[18] or the bis-amido [{Sm(Cp*)$_2$}$_2$(μ-N$_2$Ph$_2$)],[19,20] act as bifunctional initiators for the polymerization of MMA. Chain-transfer polymerization of MMA mediated by [Sm(Cp*)$_2$(Me)(thf)] and organic acids, such as thiols (most effective) or ketones has been achieved, which resulted in thienyl- and ketone-capped PMMA.[21] Other complexes, which include allyl,[22] alkyl,[23–25] lanthanocene, silylene-bridged azaallyl,[26] indenyl,[27] amido,[24,28–31] thiolato,[32] halogeno,[33–35] or divalent[31,36,37] derivatives, have been reported as efficient initiators for MMA polymerization. Noteworthy is the bimetallic bis(enolato)samarium(III) initiator, generated in situ from the coupling of a radical anion species formed by one-electron transfer from a samarocene catalyst, such as [Sm(Cp*)$_2$-(thf)$_2$], to a MMA molecule, which then opened up a route to linked-functionalized polymers.[15,17,19,20,37] Finally, diamide–diamine, guanidinate, and alkoxide monoborohydride complexes have recently been reported to initiate the polymerization of MMA with rather syndio-stereospecificity.[38–40]

Results reported with Group 3 borohydride complexes remain rather limited. By using the tetradentate dianionic ligand (2-C$_5$H$_4$N)-CH$_2$N(CH$_2$CH$_2$NSiMe$_3$)$_2$ (N$_2$NN^{SiMe_3}), Mountford and co-workers showed in preliminary studies that the monoborohydride complex [(N$_2$NN^{SiMe_3})Sm(BH$_4$)]$_2$ afforded PMMA in 50% yield with a slight syndiotactic tendency (≈52% rr; 15% mm; 33% mr), $\bar{M}_{n,exptl}$ ≈ 2.3$\bar{M}_{n,calcd}$, and $\bar{M}_w$/$\bar{M}_n$ ≈ 1.23.[38] More recently, Yuan et al. reported the monoguanidinate bis-borohydride complex [Ln(BH$_4$)$_2$-{(Me$_3$Si)$_2$NC(NCy)$_2$}(thf)$_2$] (Ln = Yb, Er) had a moderately high catalytic activity to give PMMAs in a yield of ≈39% with $\bar{M}_{n,exptl}$ ≈ 2.1$\bar{M}_{n,calcd}$ and $\bar{M}_w$/$\bar{M}_n$ ≈ 2.4 (the tacticity was not reported).[39] Temperatures higher than ambient temperature were shown to have a negative influence on $\bar{M}_n$. The presence of the borohydride was claimed to be crucial for polymerization to proceed because the homoleptic guanidinate analogues failed to polymerize MMA under similar ex-

perimental conditions. These authors also found the inorganic borohydride complex [Ln(ArO)(BH$_4$)$_2$(thf)$_2$] (Ar = C$_6$H$_2$-tBu$_3$-2,4,6; Ln = Yb, Er) was moderately active to give polymers in a yield of ≈37% with $\bar{M}_{n,exptl}$ ≈ 7.8$M_{n,calcd}$ and rather syndiotactic polymers (≈60% rr; 6% mm; 34% mr, irrespective of the reaction temperature; $\bar{M}_w$/$\bar{M}_n$ was not reported). The optimum temperature for initiator activity was around 0°C.[40] None of these borohydride initiators exhibited behavior approaching that of a controlled polymerization process, nor did they match the performances of Yasuda and co-workers' [Ln(Cp*)$_2$(H/Me)] initiators.[8–12]

To better understand the variety of results reported in the literature and to gain further information on reaction mechanisms, studies are nowadays often complemented by theoretical approaches. Indeed, such computational investigations are an invaluable tool in the elucidation of reaction mechanisms that involve a metal center;[41] this is particularly true for transition-metal-mediated reactions.[42,43] Within the last decade, the theoretical treatment of the reactivity of rare-earth-containing molecules has become possible so that reactions that involve Group 3 compounds have been successfully explored.[44,45] Theoretical contributions have allowed us to rationalize the reactivity of organolanthanide complexes and to propose original reaction mechanisms, such as the involvement of a carbene in the C−F activation of fluoromethane.[44] However, to the best of our knowledge, the role of the borohydride ligand in polymerization reactions has never been considered from a theoretical point of view.

Following our continued interest in the use of rare-earth borohydride complexes as initiators for the polymerization of polar monomers,[46–50] we have investigated acrylate monomers. Herein, we report the results of a combined experimental/synthetic and DFT-based theoretical/mechanistic study of the polymerization of acrylates initiated by the rare-earth borohydride complexes [Nd/Sm(BH$_4$)$_3$(thf)$_3$] (**1**/**2**), [Sm(BH$_4$)(Cp*)$_2$(thf)] (**3**), and Yasuda's [Sm(Cp)$_2$(H)] by using MMA as a model monomer.

Experimental Section

23 °C. The residual solvent resonance was used as the internal reference measured relative to tetramethylsilane ($\delta = 0$ ppm).

Average molar mass ($\bar{M}_n$) and molar mass distribution ($\bar{M}_w/\bar{M}_n$) values were determined by size exclusion chromatography (SEC) in THF at 20 °C (flow rate = 1 mL min^{-1}) by using a Varian apparatus equipped with a refractive index detector and three TSK HXL columns G2000, 3000, and 4000. The polymer samples were dissolved in THF (2 mg mL^{-1}). The elution curves were calibrated with PMMA standards. Monomer conversions of MMA were calculated by gravimetry.

Typical MMA polymerization: The solvent (2.5 mL) and MMA (1.5 mL, 14 mmol) were successively added to the initiator [Sm(BH$_4$)$_3$(thf)$_3$] (24 mg, 58 μmol) at the desired temperature. After the appropriate reaction time, a solution of acetic acid in toluene (0.1 mL, 1.45 mol, 14.5 × 10^3 mol L^{-1}) was added to quench the reaction and the resulting mixture was dried. The crude polymer was then dissolved in CH$_2$Cl$_2$, precipitated in cold methanol, filtered, and dried. The resulting polymer was then analyzed by NMR spectroscopy and SEC.

Computational details: All of the calculations were performed by using the Gaussian 03[53] suite of programs. For technical reasons associated with the impossibility of employing effective core potentials (ECPs) with an odd number of core electrons with Gaussian 03, the samarium atom, used experimentally, was replaced by a europium atom. Such an exchange was made previously because the calculated energy data were found to depend very little on the choice of lanthanide center.[54] Note that there were no problems with the Gaussian 98 software package. The europium atom was treated with a Stuttgart–Dresden pseudopotential, which includes the 4f core electrons, in combination with their adapted basis set.[54,55] In all cases the basis set was augmented by a set of f polarization functions.[56] Carbon, oxygen, and hydrogen atoms were described with a 6-31G(d,p) double-ζ basis set.[57] Calculations were carried out at the density functional theory (DFT) level of theory by using the hybrid functional B3PW91.[58,59] Geometry optimizations were carried out without any symmetry restrictions and the nature of the extrema (minima) was verified through analytical frequency calculations. The free energies were computed at $T = 298.15$ K within the harmonic approximation.

Results and Discussion

Polymerization of MMA initiated by [Nd/Sm(BH$_4$)$_3$(thf)$_3$] (1/2) and [Sm(BH$_4$)(Cp*)$_2$(thf)] (3)—experimental results:
The polymerization of MMA using [Nd/Sm(BH$_4$)$_3$(thf)$_3$] (1/2) and [Sm(BH$_4$)(Cp*)$_2$(thf)] (3) initiators was carried out in different solvents (THF, CH$_2$Cl$_2$, toluene) over 0.5–24 h at room temperature (Table 1). Performing the reaction at a lower temperature (−10 °C; runs 4 and 10) did not improve the activity, which suggests that thermally activated chain-termination steps are not responsible for the observed low yields and the increase in the molar masses.[13] Rather syndiotactic (≈55 % rr; 23 % mm; 22 % mr) PMMAs were obtained in low yields (≈34 %) with $\bar{M}_n$ molar masses much higher than expected ($\bar{M}_{n,exptl} \approx 21.0 \bar{M}_{n,calcd}$) and quite narrow-to-broad molar mass distributions ($\bar{M}_w/\bar{M}_n = 1.2$–2.7). Use of an organometallic complex rather than an inorganic one such as [Sm(BH$_4$)(Cp*)$_2$(thf)], which is known to improve control compared with [Sm(BH$_4$)$_3$(thf)$_3$] during the polymerization of CL thanks to its ancillary "noninnocent" ligands,[46] did not improve the overall control of the polymerization (runs 11–14). Polymer tacticity was also not improved by using an initiator with Cp* ancillary ligands. All of these results indicate that the polymerization of MMA using these borohydride initiators is not a quantitative process.

Note that the absence of impurity in MMA, which could have caused the decomposition of the borohydride initiator, has been verified by the successful polymerization of CL in the presence of an equimolar amount of MMA with [Nd(BH$_4$)$_3$(thf)$_3$]. This attempted copolymerization of CL and MMA only resulted in the formation of a polyester with the expected features ($\bar{M}_n = 5800$, $\bar{M}_w/\bar{M}_n = 1.1$);[48,50] no polyester/polyacrylate copolymer was formed. These results also revealed that polyester/polyacrylate copolymers could not be prepared from the sequential copolymerization of lactone and acrylate by using these borohydride initiators. Such copolymers have, however, been successfully synthesized from a combined ring-opening polymerization/atom-transfer radical polymerization approach by using bromo-functionalized poly(ε-caprolactone) (PCL) as macroinitiators for MMA polymerization.[60] This approach allowed the preparation of

Table 1. Polymerization of MMA initiated by [Nd(BH$_4$)$_3$(thf)$_3$] (**1**), [Sm(BH$_4$)$_3$(thf)$_3$] (**2**), or [Sm(BH$_4$)$_3$(Cp*)$_2$(thf)] (**3**).

Run	Initiator	[BH$_4$]$_0$[a] [mmol L^{-1}]	[MMA]$_0$ [mmol L^{-1}]	[MMA]$_0$/[BH$_4$]$_0$	Solvent	Temp. [°C]	Time [h]	Monomer conv.[b] [%]	$\bar{M}_{n,calcd}$[c] [g mol^{-1}]	$\bar{M}_{n,SEC}$[d] [g mol^{-1}]	$\bar{M}_w/\bar{M}_n$[e]	Tacticity,[f] rr-mm-mr [%]
1	**1**	12.5	2450	65	THF	25	4	12	780	11 000	1.6	57-16-27
2	**1**	17.8	7000	130	THF	25	4	22	2 900	17 450	2.7	51-20-29
3	**1**	12.0	2800	77	CH$_2$Cl$_2$	25	24	10	770	23 000	1.7	52-23-25
4	**1**	12	2800	77	CH$_2$Cl$_2$	−10	4	35	2 700	21 700	2.7	55-21-24
5	**1**	15.2	1300	29	toluene	25	24	7	200	11 800	1.4	52-24-24
6	**1**	5.5	1900	113	toluene	25	4	6	680	31 500	2.6	50-25-25
7	**2**	14.5	3500	80	THF	25	24	10	800	22 500	2.2	56-24-20
8	**2**	14.5	3500	80	CH$_2$Cl$_2$	25	24	11	900	15 700	2.2	51-27-22
9	**2**	6.1	2300	125	toluene	25	24	7	880	30 000	2.0	53-25-22
10	**2**	8.1	1600	67	toluene	−10	17	33	2210	32 000	2.5	55-22-23
11	**3**	10.0	3500	320	THF	25	20	100	32000	357 500	2.2	58-22-20
12	**3**	14.0	3500	250	CH$_2$Cl$_2$	25	4	30	7 500	5 000	1.2	67-18-15
13	**3**	13.7	3500	254	CH$_2$Cl$_2$	25	24	92	23 400	230 000	2.4	63-23-14
14	**3**	15.0	3500	233	toluene	25	2	95	22140	378 000	2.4	54-25-21

[a] [BH$_4$]$_0$ = 3[Nd(BH$_4$)$_3$(thf)$_3$]$_0$ = 3[**1**]$_0$, [BH$_4$]$_0$ = 3[Sm(BH$_4$)$_3$(thf)$_3$]$_0$ = 3[**2**]$_0$, or [BH$_4$]$_0$ = [Sm(BH$_4$)(Cp*)$_2$(thf)]$_0$ = 3[**3**]$_0$. [b] Monomer conversion determined by ^{1}H NMR spectroscopy analysis. [c] Calculated from [MMA]$_0$/[BH$_4$]$_0$ × 100 × monomer conversion. [d] Determined by SEC. [e] Molar mass distribution calculated from SEC chromatogram traces. [f] Determined by ^{1}H NMR analysis.

triblock PMMA-*b*-PCL-*b*-PMMA copolymers, in addition to diblocks, inaccessible from the copolymerization of MMA and CL with [Sm(Cp*)$_2$(Me)(thf)] as the initiator, which only gave the PCL-*b*-PMMA diblocks.[61]

All of the experimental data are thus consistent with poor MMA initiation efficiency of the rare-earth borohydride initiators [Nd/Sm(BH$_4$)$_3$(thf)$_3$] and [Sm(BH$_4$)(Cp*)$_2$(thf)] (**1**, **2**, and **3**). This overall behavior is similar, in terms of yield, tacticity, $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$, to that of other MMA polymerization reactions carried out by using borohydride rare-earth initiators.[38,40] It is also interesting to note that sodium borohydride is an effective polymerization inhibitor during monomer storage by reducing peroxide and hydroperoxide impurities.[62] The exceptional performances of the hydride complex [Sm(Cp*)$_2$(H)]$_2$[2,8–12] required further explanation for which we have relied on computational mechanistic investigations. These were instigated by the mechanism reported by Yasuda that suggests that the polymerization of MMA by [Sm(Cp*)$_2$(H)]$_2$ is initiated by the 1,4-addition of the hydride to the first incoming MMA molecule followed by the 1,4-addition of the resulting samarium enolate to another molecule of MMA.[2,8–12]

Polymerization of MMA initiated by [Eu(BH$_4$)(Cp)$_2$] and [Eu(BH$_4$)$_3$]—computational insights into the reaction mechanism: From a theoretical point of view, very little information is available from the literature on acrylate polymerization reactions with either lanthanide or Group 3 elements. Recently, Ziegler and co-workers reported the results of density functional theory (DFT) studies on the group-transfer polymerization of acrylates catalyzed by mononuclear early f-block metallocenes, in particular, emphasizing the mechanism of termination and transfer reactions without providing insights into the polymerization mechanism.[63,64] In this work, the influence and the role of the borohydride ligand in the polymerization of MMA was studied by investigating the reactivity of the model complex [Eu(BH$_4$)(Cp)$_2$] (Cp = η^5 C$_5$H$_5$). For practical computational reasons and for the sake of simplicity, the samarium atom in the complexes [Sm(BH$_4$)$_3$(thf)$_3$] (**2**) and [Sm(BH$_4$)(Cp*)$_2$(thf)] (**3**) used experimentally was substituted by europium and the monoborohydride organometallic derivative [Eu(BH$_4$)(Cp)$_2$] was chosen over the permethylated analogue. Indeed, it has been shown that the results (the geometry and energetics of the reactions) depend very little on the choice of lanthanide.[65] In addition, from a theoretical point of view, the absence of coordinated THF does not affect the reactivity; this has been verified in the case of Cp-type complexes. For the sake of clarity and the possibility of comparing the results, a similar assumption, maybe more approximate, has been made for the tris-borohydride complexes.

The coordination of the borohydride to the lanthanide center in [Eu(BH$_4$)(Cp)$_2$] was determined by geometry optimization and was found to be of the η^3 (trihapto) type with the three hydrogen atoms of the borohydride ligand interacting with the europium atom (Figure 1). The calculated bond distances for Eu−B (2.62 Å) and Eu−η^3H (2.33, 2.45,
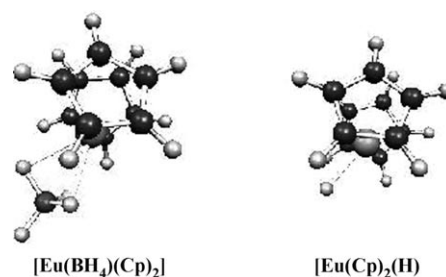

Figure 1. Optimized geometries for [Eu(BH$_4$)(Cp)$_2$] and [Eu(Cp)$_2$(H)].

and 2.46 Å) fall within the range of those obtained from X-ray structural analyses of the neutral Sm−η^3BH$_4$ complexes (2.58–2.62 and 2.28–2.51 Å, respectively).[66] This is in agreement with reports that BH$_4$ ligands in [Ln(BH$_4$)(Cp)$_2$(thf)] are bidentate in the lutetium and ytterbium analogues, but tridentate in the larger samarium derivatives, which reflects the contraction of the ionic radius.[67] Although the hydrogen atoms could not be located in the X-ray structure of [Sm(BH$_4$)(Cp*)$_2$(thf)] (**3**), tridentate complexation was expected.[68,69] Such coordination of the borohydride ligand is thus very different to the "classical" one found for the hydride so that one may expect a different reactivity, or at least a discrete mechanism, for the reaction of borohydride precursors with MMA.

The strength of the europium–borohydride interaction was determined relative to that of the hydride interaction by calculating the free energy of the reaction [Eu(BH$_4$)(Cp)$_2$]→[Eu(Cp)$_2$(H)]+BH$_3$. This reaction is endergonic by 43.10 kcal mol^{-1} so that formation of the hydride from the borohydride complex is not likely. This is, in fact, not related to the strength of the Eu−BH$_4$ bond, but rather to the instability of free BH$_3$. Comparison of the Eu− (X) calculated heterolytic bond dissociation energy (BDE) of [Eu(BH$_4$)(Cp)$_2$] (139.00 kcal mol^{-1}) with that of [Eu(Cp)$_2$(H)] (196.58 kcal mol^{-1}) and [Eu(CH$_3$)(Cp)$_2$] (185.70 kcal mol^{-1}) illustrates that the Eu−BH$_4$ bond is even weaker than the Eu−CH$_3$ bond. Thus, the 1,4-addition of the borohydride of [Eu(BH$_4$)(Cp)$_2$] to the first molecule of MMA (as observed in Yasuda's mechanism with [Sm(Cp*)$_2$(H)]$_2$), which results in the elimination of BH$_3$ along with the formation of [Eu(Cp)$_2$(H)] (in the case of Yasuda, an enolate is formed), is unlikely to occur mainly because of the low stability of free BH$_3$. Yet hydrogen transfer from the borohydride to MMA should be preferred, and thus, lead to the formation of an enolate compound. Therefore, all of the reactions involving B−H activation have been considered in the calculations, namely, enolate formation, carboxylate formation, and hydroboration of the double bond. Both the first 1:1 adduct of [Eu(BH$_4$)(Cp)$_2$]/MMA and the first MMA insertion product (the rate-determining step of the polymerization reaction) have been studied by DFT calculations.

Addition of MMA to [Eu(BH$_4$)(Cp)$_2$] initially results in the coordination of MMA to the metal center to form the solvated complex [Eu(BH$_4$)(Cp)$_2$(MMA)] for which differ-

ent minima were found on the potential energy surface (PES). The lowest of these minima always involve the coordination of MMA through the oxygen of the carbonyl group because these oxygen lone pairs are more accessible for coordination than, for instance, the C=C double bond. In the case of carbonyl oxygen coordination, the four minima identified correspond either to a lateral or to a geminal orientation of the MMA molecule relative to [Eu(BH$_4$)(Cp)$_2$], as illustrated in Figure 2. Calculations on the coordination of the first MMA molecule to [Eu(BH$_4$)(Cp)$_2$] revealed that all carbonyl-bonded adducts are exergonic, and adducts **a** and **c** are the most stable (by 3.87 and 4.11 kcal mol^{-1}, respectively).[70] The main difference between **a** and **c** is that either the CH$_2$ (**a**) or the OMe (**c**) group is pointing towards the hydride, and thus, different reactivities can be predicted for the two adducts.

We then analyzed the thermodynamics of the reactions and considered the kinetics by calculating the activation barrier of the transition state (TS) when appropriate. A schematic of the thermodynamic results for the reactions of [Eu(BH$_4$)(Cp)$_2$] with MMA is given in Figures 3 and 4. The enolate [Eu(Cp)$_2${O(OMe)C=C(Me)$_2$}] (**e**) formation reaction, which occurs by BH$_3$ elimination, is calculated to be endergonic by 11.98 kcal mol^{-1} so this reaction is thermodynamically forbidden (for this reason, the TS has not been optimized), possibly because of the low stability of the free BH$_3$, as highlighted above. The instability of the uncomplexed BH$_3$ is further evidenced when considering the possible coordination of the BH$_3$ formed to the enolate intermediate (**e**). Two minima, **e-1** and **e-2**, are found on the PES (Figure 4). In the first minimum, the BH$_3$ molecule adds to the Cp ring to give an enolate [Eu(Cp)(CpBH$_3$){O-(OMe)C=C(Me)$_2$}] (**e-1**) that is more stable than **e**, yet its formation is still endergonic by 8.14 kcal mol^{-1}. The second minimum, in which BH$_3$ adds to the oxo group [Eu(Cp)$_2$-{(OBH$_3$)(OMe)C=C(Me)$_2$}] (**e-2**), is thus better described as a complex with a borate ligand that interacts with the lanthanide center rather than as an enolate complex. Direct formation of **e-2** by hydrogen transfer from BH$_4^-$ to =CH$_2$ (Figure 3i) first requires the formation of
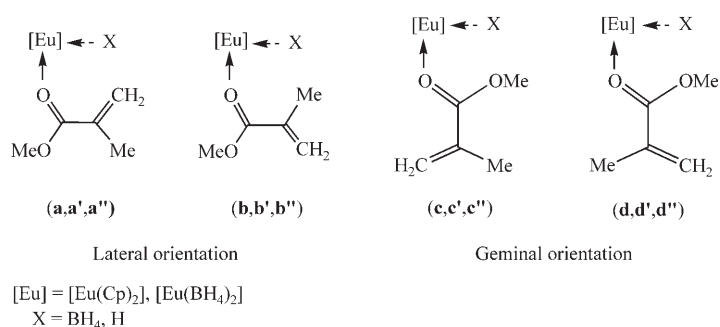

[Eu] = [Eu(Cp)$_2$], [Eu(BH$_4$)$_2$]
X = BH$_4$, H

Figure 2. Possible MMA adducts with the [Eu(Cp)$_2$(X)] (X=BH$_4$, H) and [Eu(BH$_4$)$_3$] complexes.

enolate **e** and then both the rotation of the enolate and BH$_3$ addition to be kinetically accessible. Complex **e-2** is much more stable than the other two enolates (**e** and **e-1**) and the formation reaction is exergonic by 8.12 kcal mol^{-1}. Therefore, as this reaction is thermodynamically favored, a small amount of **e-2** might be obtained via intermediate **e**, even though the formation of **e** is endergonic. We previously en-
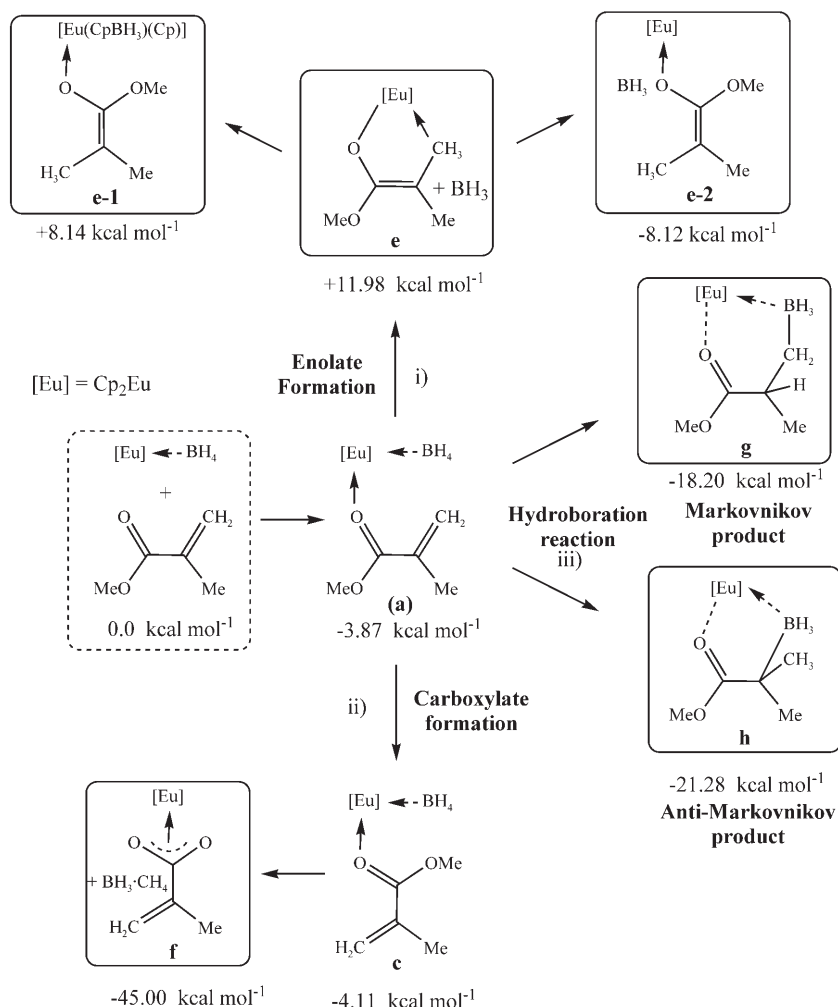

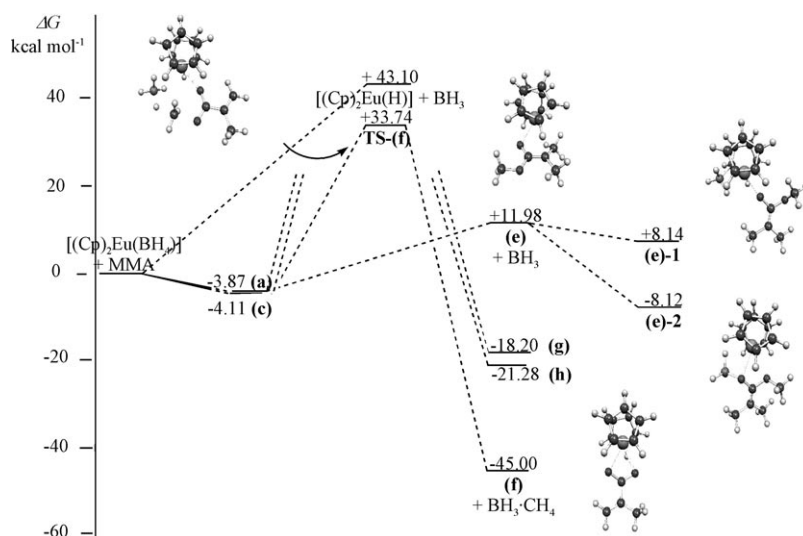Figure 3. Schematic of the thermodynamic results for the reactions of [Eu(BH$_4$)(Cp)$_2$] with MMA.

Figure 4. Calculated free-energy profile for the reaction of MMA with $[Eu(BH_4)(Cp)_2]$.

countered a similar situation for the formation of benzyne from $[Ce(Cp_2)(C_6F_5)]$; this involves an endergonic step before the exergonic Ce−F formation.[45] Thus, borate complex **e-2** might then initiate the polymerization of MMA, yet, according to Yasuda's mechanism, the subsequent MMA insertion should lead to an enolate complex that requires cleavage of the borate–lanthanide interaction, but which should not, in principle, imply formation of unstable free BH_3. Therefore, even if the polymerization of MMA takes place to some extent through active species **e-2**, the formation of **e-2** from $[Eu(BH_4)(Cp)_2]$ and MMA is certainly not quantitative and results in a poorly controlled polymerization process, as observed experimentally. Note, although rare-earth alkoxides, such as $[Sm(C_5Me_5)_2(OEt)-(Et_2O)]$,[71] $[Sm(C_5Me_5)_2(OBu)(thf)]$,[71] or $[La(OiPr)_3]$,[72] do not initiate the polymerization of MMA, rare-earth enolate complexes, which are often generated in situ by addition of MMA, have been reported to be efficient initiators for the polymerization of MMA.[13,17,19,28,73,74]

The formation of the carboxylate $[Eu(Cp)_2\{OOC−C(Me)-(=CH_2)\}]$ (Figure 3i) is found to be thermodynamically favorable, but kinetically disfavored, with respect to enolate formation (Figure 4). This reaction is highly exergonic (45.00 kcal mol^{-1}), which clearly demonstrates that the lanthanide–carboxylate interaction is stronger than the lanthanide–borohydride interaction (Figure 4). Indeed, even though the strong lanthanide–borohydride interaction is hard to break, it has to be broken and is definitely disrupted in this process, the driving force of the reaction is the formation of **f** along with the liberation of $BH_3 \cdot CH_4$. As the reaction is thermodynamically favorable, the corresponding transition state **TS-f** is located on the PES (Figure 4). This TS appears to arise from a nucleophilic substitution (S_N) reaction in which the CH_3 group migrates from O$^-$ to BH_4^-. The activation barrier is calculated to be quite high (+33.74 kcal mol^{-1}) so the reaction is kinetically difficult and unlikely to occur. Thus, MMA polymerization is unlikely to be initiated

by carboxylate intermediate **f**. MMA polymerization initiated by a rare-earth carboxylate complex has, to the best of our knowledge, never been reported. $[Sm(C_5Me_5)_2(OCOCH_3)]$ has been declared to be incapable of initiating the polymerization of MMA.[71]

The hydroboration of the double bond may lead to two species: Either the Markovnikov $[Eu(Cp)_2\{O(OMe)C−CH(Me)(CH_2BH_3)\}]$ (**g**) or the anti-Markovnikov $[Eu(Cp)_2\{O-(OMe)C−C(Me_2)(BH_3)\}]$ (**h**) product (Figure 3). Both reactions are calculated to be exergonic by 18.20 and 21.28 kcal mol^{-1}, respectively (Figure 4), which may simply be explained by the formation of a borane strongly interacting with the lanthanide center. From a kinetic point of view, despite our efforts, it has not been possible to locate any transition states. Indeed, because the borohydride in the TS no longer has to interact with the lanthanide center, the TS should be quite high in energy. Neither of the hydroboration products (**g**, **h**) may initiate the polymerization of MMA because the boranes exhibit an aliphatic carbon chain rather than a classical unsaturated one. This would indeed make subsequent MMA insertion as difficult as the initial one; the borane–lanthanide interaction would need to be broken to form the enolate, which would result in the liberation of free BH_3.

As the experimental work also concerned the tris-borohydride $[Ln(BH_4)_3(thf)_3]$ complexes, the geometries of the most stable species found with $[Eu(BH_4)(Cp)_2]$ were optimized by using $[Eu(BH_4)_3]$ as a model. An overall behavior similar to that described for the organometallic derivative is observed, and the geometries of the complexes are very similar and all of the thermodynamic values are exergonically shifted towards greater stability (Figure 5).[70] Enolate **e′** is thermodynamically unfavorable (+10.33 kcal mol^{-1}) whereas the formation of borate **e′-2** is exergonic (−14.45 kcal mol^{-1}).

The extra stabilization of enolates **e′** and **e′-2** compared with the $[Eu(BH_4)(Cp)_2]$ case was calculated to be 1.65 and 6.33 kcal mol^{-1}, respectively. In the same way, the formation of carboxylate **f′** is calculated to be exergonic by 55.72 kcal mol^{-1} (extra stabilization of 10.72 kcal mol^{-1}) and the formation of hydroboration products **g′** and **h′** is also exergonic by 28.32 and 28.37 kcal mol^{-1}, respectively (extra stabilization of 10.12 and 7.09 kcal mol^{-1}, respectively). The overall energetic situation for the tris-borohydride complex is thus similar to that of the monoborohydride organometallic derivative, but all of the reactions investigated appear to be easier with the $[Eu(BH_4)_3]$ complex. In fact, $[Eu(BH_4)_3]$ exhibits a stronger Eu–BH_4 interaction than $[Eu(Cp)_2(BH_4)]$, as determined by the Eu−BH_4 BDE value, which is higher in
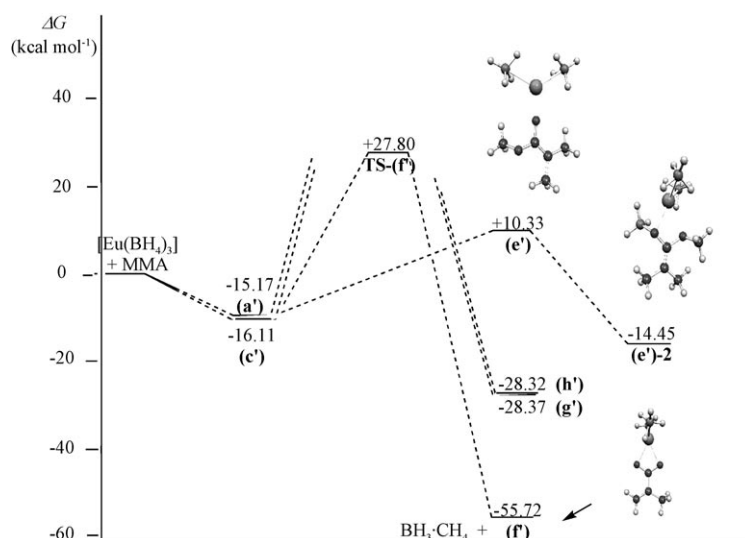
Figure 5. Calculated free-energy profile for the reaction of MMA with [Eu(BH$_4$)$_3$].

$[Eu(BH_4)_3]$ (174 kcal mol^{-1}) than in $[Eu(BH_4)(Cp)_2]$ (139 kcal mol^{-1}). This is in agreement with the fact that a Cp$^-$ ligand is more electron-donating than a BH$_4^-$ one and thus the Eu−BH$_4$ interaction is stronger in $[Eu(BH_4)_3]$ than in $[Eu(BH_4)(Cp)_2]$; the lanthanide center is less acidic in the latter case and leads to a weaker electrostatic interaction with the borohydride. Moreover, the steric hindrance around the lanthanide center is smaller within the [Eu-(BH$_4$)$_2$] fragment than within the [Eu(Cp)$_2$] one. Thus, the borohydride ligand may interact over a longer distance in the latter organometallic fragment than in the former one, thereby reducing the strength of the electrostatic interaction. Thus, all reactions that involve the formation of an electrostatic interaction between MMA and the metal center, such as in enolate e-2, carboxylate f, or hydroboration products g and h, will be thermodynamically more favorable for the tris-borohydride complex than for the organometallic one. These findings reveal that the ancillary ligands, which often play a significant role in improving the control of polymerization reactions,[5–7,47] may have opposite (negative) inputs into the thermodynamics and kinetics of the real active species.

Thus, These DFT investigations reveal that the reaction of $[Eu(BH_4)(Cp)_2]$ or $[Eu(BH_4)_3]$ with one MMA molecule probably leads to enolate e-2 or e′-2 via intermediate e or e′, the other potential products are very unlikely because of either an endergonic pathway in the case of enolate e-1 or e′-1, or a TS too high in energy in the case of the hydroboration (g, h, g′, and h′) and the carboxylate (f and f′) products. Therefore, even if the polymerization of MMA takes place to some extent through the active species e-2 or e′-2 (species f, g, h, f′, g′, and h′ being extremely unlikely to initiate the polymerization), the formation of e-2 or e′-2 from [Eu-(BH$_4$)(Cp)$_2$] or [Eu(BH$_4$)$_3$] and MMA is certainly not quantitative and results in a poorly controlled polymerization process. This is in agreement with experimental observations

because, in addition to being uncontrolled, hardly any polymerization occurred with the borohydride complexes [Ln-(BH$_4$)$_3$(thf)$_3$] (Ln=Nd, Sm) or [Sm(BH$_4$)(Cp*)$_2$(thf)]. These findings suggest that, upon further comparison with the organometallic initiating complexes used by Mountford and Yuan, the ligands surrounding the metal play a significant role in improving (to some extent) the control of the polymerization.[38,39,40] A good compromise between the steric, electronic, kinetic, and thermodynamic contributions of the ligands still remains to be reached for a Group 3 initiator to be efficient in MMA polymerization.

Polymerization of MMA initiated by [Sm(Cp)$_2$(H)]$_2$—computational insights into Yasuda's reaction mechanism: To gain further insights into why the borohydride complexes are far from being as efficient in the polymerization of MMA as Yasuda's hydride or alkyl initiators [Sm(Cp)$_2$(H/CH$_3$)]$_2$, we investigated the mechanism proposed by Yasuda by DFT by using [Eu(Cp)$_2$(H)] as a model to obtain information on the importance and on the different mode of action of the borohydride ligand. Indeed, even though the original complex is dimeric, the active species is known to be the monomeric lanthanide hydride complex.[2,8–12] Yasuda suggested that in the initiation step, the hydride should attack the CH$_2$ group of MMA to generate a transient [Sm-(Cp*)$_2${OC(OMe)=C(Me)$_2$}] species and then the second incoming MMA molecule should participate in a 1,4-addition to afford an eight-membered ring enolate intermediate. This key intermediate, which is the active species in the syndiospecific polymerization of MMA, has been isolated from the 1:2 reaction of [{Sm(Cp*)$_2$(H)}$_2$] with MMA and further characterized by its X-Ray structure.[2,8–12]

Coordination of the first MMA molecule to [Eu(Cp)$_2$(H)] to form [Eu(Cp)$_2$(H)(MMA)] gives, similarly to the borohydride case, four minima that all exhibit carbonyl oxygen coordination to the metal (Figure 2). These adducts are similar in energy, but adducts a″ and c″ are the most stable (c″ is slightly more stable than a″) and almost degenerate (exergonic by 5.81 and 5.90 kcal mol^{-1}, respectively; Figure 6).[70] As isomerization between a″ and c″ is not so trivial, reaction pathways starting from both of these adducts have been investigated.

The thermodynamic results for the reactions of [Eu(Cp)$_2$(H)] with MMA are shown in Figure 6. Two different pathways that lead either to enolate e″ or carboxylate f″ have been determined. The formation of the enolate

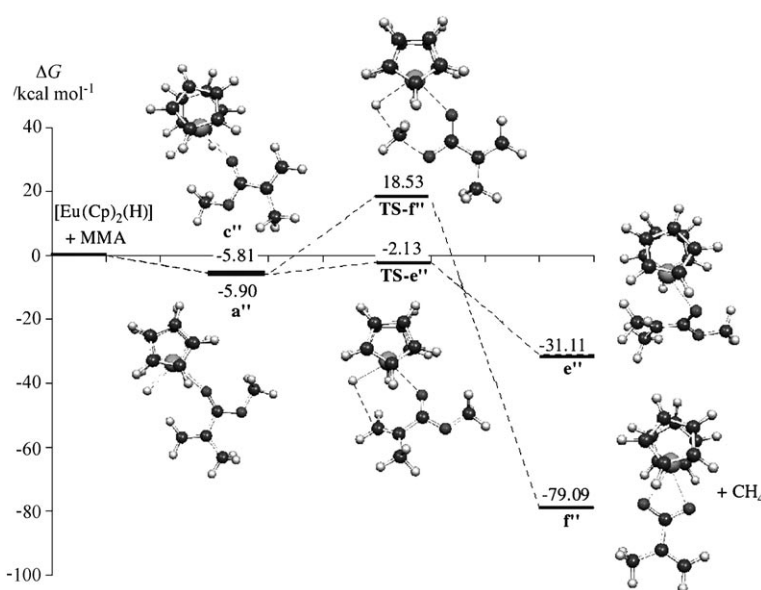Figure 6. Calculated free-energy profile for the reaction of MMA with [Eu(Cp)₂(H)].

though this reaction is clearly thermodynamically favored, the formation of carboxylate **f″** is kinetically so difficult that instead the formation of enolate **e″** is much more likely. These computational results are in agreement with both Yasuda's experimental observations and his reported mechanism for the polymerization of MMA with [Sm(Cp*)₂(H)]₂ as the initiator,[2,8–12] and further reveals that the formation of enolate [Eu(Cp)₂{O(OMe)C=C(Me)₂}] (**e″**) is under kinetic control. Calculations on subsequent MMA addition also show that the first MMA addition, which leads to the formation of enolate **e″**, is in fact the determining step in the polymerization of MMA with [Eu(Cp)₂(H)] as the initiator.

[Eu(Cp)₂{O(OMe)C=C(Me)₂}] (**e″**) according to Yasuda's mechanism is calculated to be exergonic by 31.11 kcal mol⁻¹ and involves first the formation of adduct **a″** which is also exergonic by 5.81 kcal mol⁻¹. The 1,4-addition of the Eu–H functionality to MMA then takes place through a TS displaying, as expected, a low activation barrier (−2.13 kcal mol⁻¹). Such behavior has already been observed in the case of the 1,3-butadiene insertion into [Nd(Cp)₂(H)] by Perrin et al.[75] Thus, the reaction that leads to the formation of enolate **e″** is calculated to be both kinetically and thermodynamically accessible. This is an important difference between the borohydride [Eu(BH₄)(Cp)₂] and the analogous hydride [Eu(Cp)₂(H)] initiators as in the former case the formation of enolate **e** is thermodynamically disfavored. With the borohydride complex, the final product issued from the reaction of [Eu(BH₄)(Cp)₂] with MMA is the borate derivative [Eu(Cp)₂{(OBH₃)(OMe)C=C(Me)₂}] (**e-2**) and not the enolate [Eu(Cp)₂{O(OMe)C=C(Me)₂}] (**e**). This result is quite interesting because, as mentioned before, the Eu–H bond is calculated to be stronger than the Eu–BH₄ one. Thus, even though the bond is slightly weaker in the borohydride case, the formation of enolate **e** is controlled by the liberation of BH₃, which prevents the formation of the enolate, thereby favoring borate derivative **e-2**.

The reaction of [Eu(Cp)₂(H)] with MMA that leads to the formation of the carboxylate [Eu(Cp)₂{OOC–C(Me)(=CH₂)}] (**f″**) complex along with methane elimination proceeds first through the formation of adduct **c″** (Figure 6). This reaction is calculated, as in the case of [Eu(BH₄)(Cp)₂], to be very exergonic (−79.09 kcal mol⁻¹) and is thus thermodynamically favored. However, the reaction occurs through quite a high-energy TS of S_N type with an activation barrier of +18.53 kcal mol⁻¹. This high value is simply explained by the formation of a planar CH₃ group in the TS such that the reaction takes place by nucleophilic substitution. Thus, even

Replacing H by BH₄ in [Eu(Cp)₂(X)] (X=BH₄, H) thus seems to prevent the 1,4-addition of the borohydride to the first incoming MMA molecule, but favors the formation of the borate complex [Eu(Cp)₂{(OBH₃)(OMe)C=C(Me)₂}] (**e-2**). The enolate [Eu(Cp)₂{O(OMe)C=C(Me)₂}] (**e″**) formed from Yasuda's hydride complex is more likely to induce the polymerization of MMA than the borate **e-2**, as has indeed been observed experimentally.

Conclusion

Through this study we have explored the polymerization of MMA initiated by [Ln(BH₄)₃(thf)₃] (Ln=Nd, Sm) or [Sm(BH₄)(Cp*)₂(thf)] and correlated the experimental results to the mechanism investigated by DFT based on the borohydride and hydride precursors [Eu(BH₄)₃], [Eu(BH₄)(Cp)₂], and [Eu(Cp)₂(H)]. From our calculations, the active species formed upon reaction of the metallic precursor with the first MMA molecule, in the case of the borohydride complexes [Eu(BH₄)₃] and [Eu(BH₄)(Cp)₂], is a borate formed via an enolate. Yet the energy barrier involved in this process might limit its formation, and thus, lead to uncontrolled polymerization, as observed experimentally. The effect of the ancillary rare-earth ligands, evaluated by comparing [Eu(BH₄)(Cp)₂] with [Eu(BH₄)₃], revealed that the two Cp ligands increased the energy values and thus decreased the stability of all the products considered. Enolate formation is, however, more energetically favored in the reaction of [Eu(Cp)₂(H)] with MMA, and therefore, allows subsequent polymerization of MMA in a well-controlled manner, as already reported experimentally by Yasuda for [{Sm(Cp*)₂(H)}₂].

This study has also shown that computational chemistry has an increasing role to play in chemistry and especially in the elucidation of reaction mechanisms, which enables one to obtain valuable information otherwise inaccessible and to perform chemistry with a different approach. This first pioneering DFT study on a polymerization mechanism involving borohydride complexes as precursors to initiators has played a significant role in elucidating the reaction mechanism and has allowed the experimental results to be rationalized. Other behavior of borohydride derivatives in polymerization mechanisms is currently under investigation.

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[70] Adduct **b** = −2.50 kcal mol^{-1}, **d** = −3.37 kcal mol^{-1}; as only adducts **a** and **c** led to products, adducts **b′**, **d′**, **b″**, and **d″** were not considered.

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