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Evaluation of the Potential of $[\{Me_2C(Cp)_2\}Zr(Me)]^+$ and $[\{Me_2C(Cp)_2\}Zr(H)]^+$ as Single-Site Catalysts for Controlled Methyl Vinyl Ether Polymerizations by Density Functional Calculations

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Density functional calculations were carried out on the B3LYP level of theory to study the initiation and propagation steps of polymerization of methyl vinyl ether (MVE) using $[Me_2C(Cp)_2Zr(Me)]^+$ and $[Me_2C(Cp)_2Zr(H)]^+$ as catalysts. From the obtained results it is concluded that initiation is possible in general with $[Me_2C(Cp)_2Zr(H)]^+$ as the catalyst and unlikely to happen with $[Me_2C(Cp)_2Zr(Me)]^+$. Also with $[Me_2C(Cp)_2Zr(H)]^+$ active propagation channels were found, which generally render the polymerization possible. However, the range of suitable reaction conditions appears to be so narrow that subtleties, which cannot be treated easily in a computational study, might still prevent polymerization. Furthermore, inactive but not irreversible propagation paths were found, which lead to species that are favored energetically compared to species in active reaction channels. This finding also hints at a successful polymerization to be problematic but not necessarily impossible. Also, the search for a catalyst precursor compound—which was located as $[Me_2C(Cp)_2Zr(H)(Ph)]$—was successful.

Introduction

Zirconocene catalysts have found widespread application in the polymerization of nonpolar olefins such as ethylene and α-olefins.[1] Also, polar olefins such as methyl methacrylate (MMA) were polymerized successfully with different zirconocene-based multi- or monocomponent catalyst systems.[2,3] Part of the impressive success of zirconcenes in this field is the possibility to create stereoselective catalysts by carefully choosing the appropriate ligand system. The elucidation of reaction mechanisms by computational studies has helped profoundly in understanding how stereoselective polymers are generated by these catalysts.[4] Recently we were able, on the basis of computational studies, to suggest a mechanism for the stereoselective polymerization of MMA.[5] From the insights obtained, we found it tempting to predict, by means of theoretical calculations, the possibility of polymerizing methyl vinyl ether (MVE) using single-component/single-site zirconocene catalysts—an aim which, to our knowledge, has been addressed neither experimentally nor computationally. It would be of interest to meet this challenge, since a controlled polymerization by single-site zirconocene catalysts could generally open the way to the design of stereoselective polymerization of MVE, which also has not been reported about so far. A future goal would be the synthesis of highly syndiotactic or highly isotactic poly-MVE, which could be expected to enrich the range of material properties of MVE polymers.

The polymerization of MVE is usually accomplished by cationic polymerization initiated, for instance, by protonic or Lewis acids.[6] Also, titanocene-based catalysts were used in conjunction with coinitiators.[7] A controlled single-site polymerization of MVE with zirconocenes is of interest, since zirconocenes with appropriate ligand systems allow for stereoselective polymerization, for instance, of propylene or methyl methacrylate, and given the structural similarities of propylene and MVE it might be possible to apply these ligands for stereoselective MVE polymerization. The first question consequently is as follows: do the energetics of the potential hypersurface of such a system allow or prevent a polymerization of MVE in general? We set out to calculate a representative amount of

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stationary points of a hypersurface of this kind, on which we report here. In this work we only address a single-component zirconocene catalyst system, with no cocatalysts or other activators. We shall deal with initiation and propagation in separate subsections and also extend the investigation to find precursors suitable for generation of the active species. The calculations presented herein do not account for counterion effects, which is justified as long as in experimental work noncoordinating counterions as BPh_4^- would be used. The influence of counterions or other compounds present in the reaction mixture is addressed in more detail in the last subsection.

Computational Details

All calculations were carried out using the Gaussian98 program package.[8] We chose the B3LYP level of theory and used the 6-31G(d) basis set as is implemented in Gaussian98 for elements C, N, O, and H in combination with the DZVP basis set for Zr developed by Godbout et al.[9] to give basis set 1 (B1). The quality of this calculation method was checked before, by comparison of crystal structures of real molecules with calculated ones.[10] Geometry optimizations were carried out with no constraints or restraints, and all geometries were checked by frequency calculations to prove if they were local minima on the potential hypersurface (zero imaginary frequencies) or saddle points of order 1 for transition states (one imaginary frequency). All transition states were used as input for IRC calculations to successfully prove that the transition state obtained does indeed connect the correct reactants and products (there is one exception to this, which is explicitly mentioned in the text). Table 1 of the Supporting Information lists the energies obtained. The discussion in the text is generally based upon calculated uncorrected energies. However, Gibbs free energies are also used for discussion, which is mentioned in the text.

Alternative Initiation Reactions

In analogy to zirconocene-catalyzed polymerizations of ethylene and MMA, we started out with the cationic Zr complex $[\{Me_2C(Cp)_2\}Zr(Me)]^+$ (**1**) as the active species (Scheme 1, Figure 1). Three different ways of adding MVE to **1** were studied, taking into account different regiochemistry: (i) coordination of MVE to **1** via the ether oxygen atom, resulting in the formation of **2**, (ii) olefin coordination of MVE to **1**, yielding **3**, in which the OMe group of MVE is oriented away from the zirconium-bound methyl group (the C−C double bond being parallel to the Me−Zr−C_{bridge} plane), and (iii) coordination via the olefinic group in its reversed orientation, yielding **4** with the OMe group oriented to the zirconium-bound methyl group (a compound with an orientation of the olefinic double bond perpendicular to the Me−Zr−C_{bridge} plane was searched for but could not be located).

All three reactions yield clearly exothermic products (**2**, −31.31 kcal/mol; **3**, −28.36 kcal/mol; **4**, −28.80 kcal/mol). Upon formation of **2** the C−C double bond of the coordinated MVE molecule is slightly shortened (1.327 Å; Figure 1) compared to free MVE (1.333 Å). This is a result of the higher electron demand of the oxygen atom (which is donating part of its electrons to the metal center), which in turn weakens the O−C1 bond (1.409 Å compared to 1.363 Å in free MVE). This is compensated for by the C2 atom moving closer to the C1 carbon. However, when **3** is formed, the C−C double bond is lengthened to 1.368 Å (Figure 1), indicating its weakening and interacting with the metal center, and different from the case for coordinated ethylene (for comparison see compounds **E1**, **E2**, and **TSE1-E2** in the insert in Scheme 1 and Figure 1), the MVE molecule is attached much more asymmetrically to the zirconium center, with the C2 atom being substantially closer (2.571 Å) to it than the C1 atom (3.203 Å), reflecting the higher electron density at C2 compared to C1. These differences are also obvious in **4** (Figure 1).

When the methyl group of **2** is transferred to the C2 atom of the coordinated MVE complex **5** is formed, in which the new Zr−C bond is slightly longer (2.289 Å) than the Zr−CH_3 bond was in **2** (2.273 Å). However, the ether oxygen atom in **5** contributes significantly to the coordination of the zirconium center, which is reflected by a Zr−O distance of 2.205 Å. Complex **5** is more stable than **2** by −7.28 kcal/mol. Unfortunately, **5** will not be formed directly from **2**, since the energy of the corresponding transition state **TS2-5** amounts to +62.37 kcal/mol, which is far too high to consider this a realistic pathway of the reaction.

If the methyl group of **3** is transferred to the C2 atom of MVE, yielding **6**, the energetics are quite different. Here the product (**6**) is an endothermic compound (+7.10 kcal/mol), and the energy of the transition state **TS3-6** (+24.53 kcal/mol) is substantially lower. However, this activation energy lies in a range which is intermediate between activation energies which hint at reactions that are easily accomplished and reactions which most certainly will not occur. The reaction would run safely if **6** were able to rearrange to **5**: the activation energy for this process is only +4.32 kcal/mol, and **5** would be formed in an exothermic reaction (−17.07 kcal/mol relative to **6**). However, it is not unequivocally clear if this reaction will work, which makes this approach somewhat unfortunate. We should mention in this context that for reasons of comparison we calculated the methyl transfer step for ethylene and found an exothermic product (−7.97 kcal/mol) and a low-lying transition state (+7.72; cf. insert in Scheme 1 and Figure 1). Upon examination of the methyl transfer starting from **4**, it turns out that the product **7** is endothermic by approximately the same amount as **6**. It is interesting to note that no transition state for this reaction could be located; thus, the reaction cannot start via this sequence. When the Gibbs free energies of the

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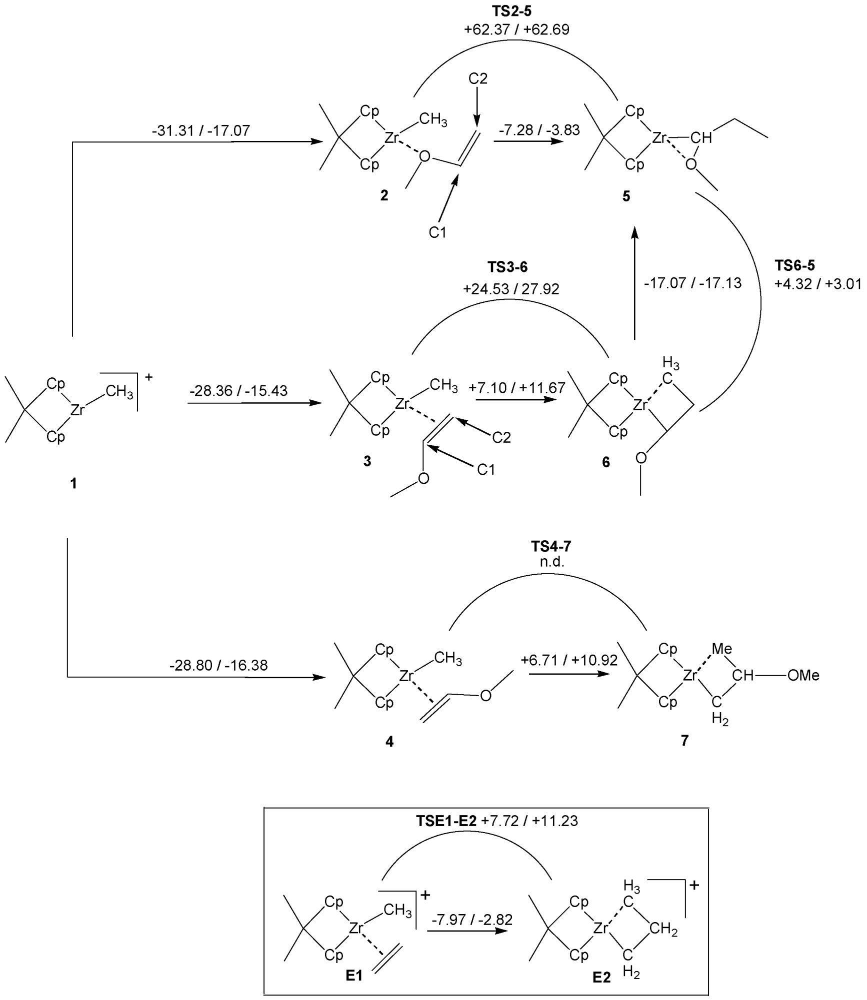
Scheme 1. Energy Profiles for Initiation Using 1 as Active Species[a]



[a] All zirconocenes shown are monocations; for clarity the charge is only indicated for **1**. Values above straight reaction arrows denote the stability in internal energy *E* and Gibbs free energy *G* (*E*/*G*; kcal/mol) of the corresponding product relative to the reactant. Values above curved arrows denote the stability (*E*/*G*; kcal/mol) of the corresponding transition state relative to the reactant. The insert shows the same reaction sequence calculated for ethylene.

compounds studied in this subsection are used for evaluation, the same conclusions can be drawn. In the next step we investigated whether a 5-fold-coordinated zirconium center can play a role in initiation, which can be ruled out (the results of this substudy are summarized in the Supporting Information).[11]

At this point, the only energetically possible initiation sequence proceeds via **3** and **6** to **5**; however, an alternative with lower activation energy is desirable. Thus, we looked for a better way of initiation. If it were possible to find a catalyst that does not contain a methyl group to be transferred, but a group with less electron donating power than that of the new Zr−C bond to be formed in the first reaction step, chances should be better to lower the activation energies for the transfer of this substituent. Zirconocene hydrides are known to insert hexene readily,[12] which prompted us to investigate the reaction behavior of a zirconocene hydride.

In Scheme 2 the energetics of the three fundamental insertion steps are outlined, and in Figure 2 the calculated structures are shown. Adding MVE to **H1** via the oxygen atom of the MVE molecule leads to **H2** in a strongly exothermic reaction (−37.02 kcal/mol). Also, the transfer of the zirconium-bound hydrogen of **H2**, yielding **H3**, is easily possible from the energetical viewpoint: **H3** is not only a clearly exothermic product (−11.73 kcal/mol), but more important, the transition state **TSH2-H3** requires only an energy of +7.46 kcal/mol. This energy profile is very similar to that obtained before for the ethylene polymerization (vide supra). Interestingly, the olefinic double bond of **H2** is elongated notably (1.343 Å) and, compared to **2**, both the C1 and the C2 atom are substantially closer to the metal center of **H2**, reflecting its higher electron demand. Also, the coordination of the zirconium center in the transition state **TSH2-H3** (Figure 2) deserves a comparison with the structural features of **TS2-5** (Figure 1): in **TSH2-H3** the metal's coordination sphere consists of the oxygen atom, both carbon atoms, and the hydrogen. In **TS2-5** only the oxygen, the neighboring carbon atom, and the departing methyl group coordinate the metal center. The Mulliken charges of the zirconium center

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[11] At this time, we have not applied this approach in detail to **3** and **4**, for which it also could be possible to take up one more MVE molecule before transferring the methyl group. However, preliminary calculations show that, as for **2** + MVE, one obtains isolated **3** and **4** together with an unbound MVE molecule.

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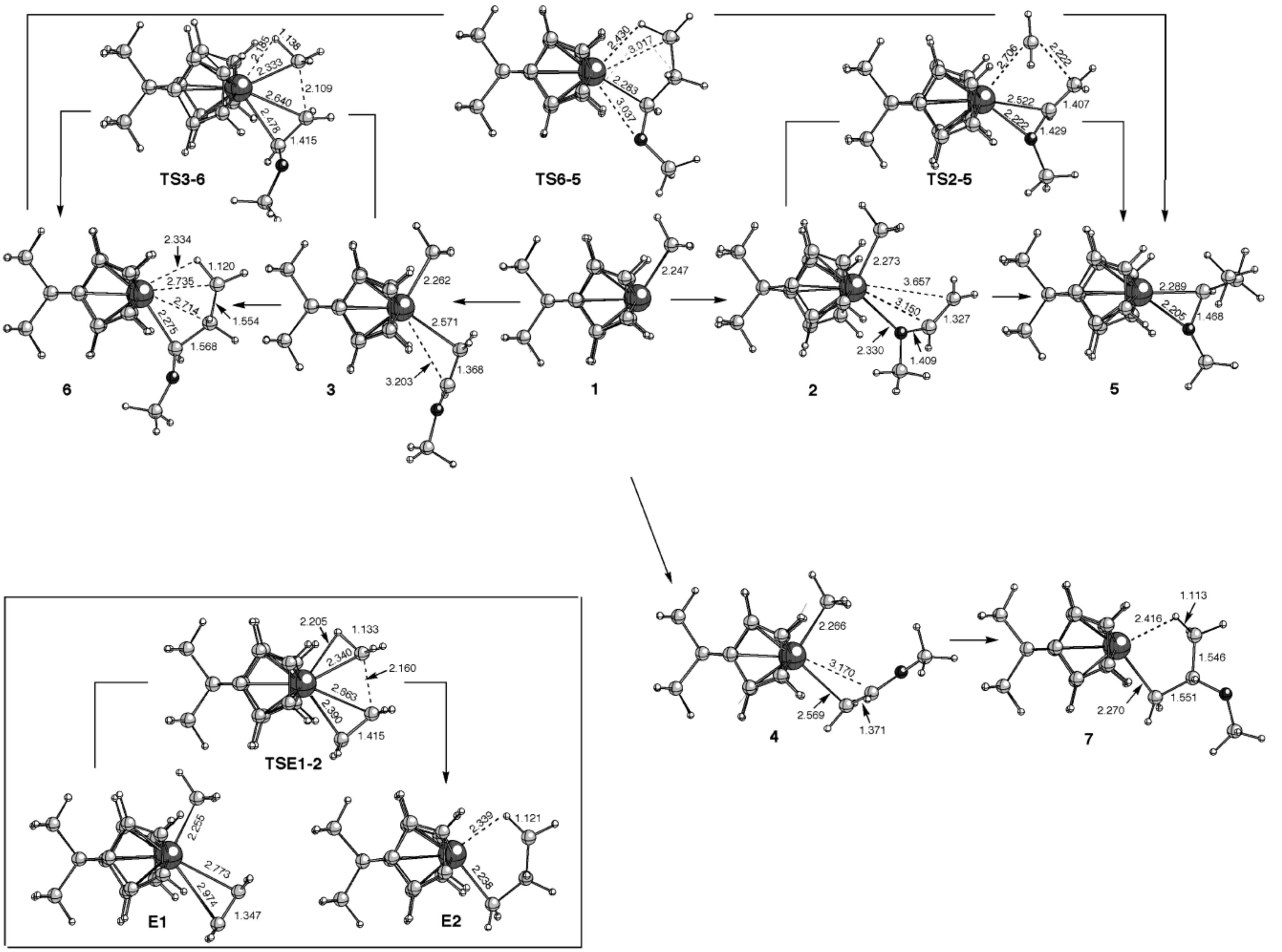


Figure 1. Calculated structures of molecules involved in the initiation via **1** (atom distances in Å; atoms in decreasing size Zr, C, O, H). The insert shows the structural features for the initiation of ethylene polymerization, calculated for comparison.

reflect this. In **TSH2-H3** the charge is +0.41, whereas in **TS2-5** it is +0.58; i.e., in **TSH2-H3** the charge on the metal is lower, since the C2 atom is always close enough to the metal to coordinate to it. This is part of the explanation why the energy of **TSH2-H3** is considerably lower than that of **TS2-5**.

However, reaction of **H4** in which the olefinic double bond coordinates to the zirconium center to **H5** also is possible at a first glance. **H5** is slightly endothermic (+1.25 kcal/mol), but unexpectedly the reaction proceeds without activation energy (also the obtained transition state structure was identical with that obtained for the reaction of **H2** to **H3**). However, we found the IRC calculation starting from **TSH4-H5** not to complete satisfactorily, and more detailed studies (which are summarized in the Supporting Information) showed that the initiation sequence **H4-H5** is doubtful. As will be shown below, this result most probably does not influence the overall reaction.

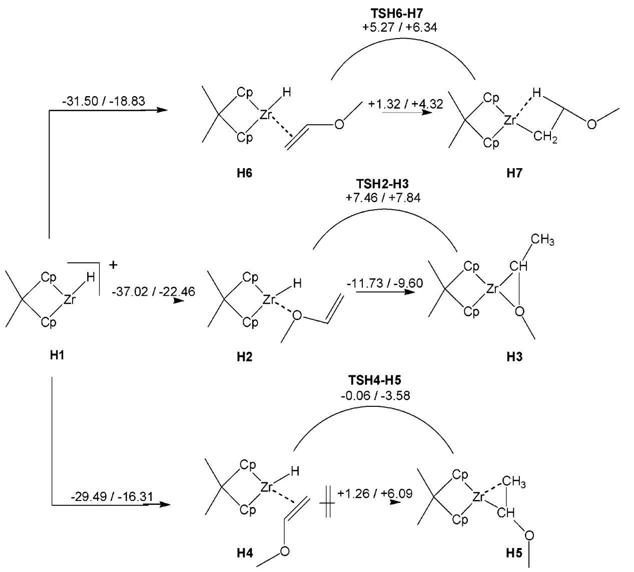
The third reaction proceeding via **H6** to **H7** again is possible in general. The reaction product is slightly endothermic by +1.32 kcal/mol, but more important is the activation energy for this reaction, which is only +5.27 kcal/mol greater than the energy of the reactant. Also in this subsection the Gibbs free energies do not alter the overall picture obtained.

From these results it follows that the transfer of hydrogen is energetically clearly advantageous over the transfer of a methyl group and more than one reaction sequence seems to be possible. Before addressing the propagation steps, we searched for a precursor which could serve as a starting material for this polymerization.

The Search for a Precursor

Which compound can be employed as a precursor? At first we investigated whether MVE is capable of replacing the NBu_3 ligand in the hypothetical complex $[\{Me_2C(Cp)_2\}Zr(H)(NBu_3)]^+$ (**8**)[13] (Scheme 3). It turns out that the reaction of **8** with MVE is endothermic as far as the formation of **H6** is concerned; only the tranformation to **H2** is exothermic. This result does not mean that **H6** will not be formed but that **H2** will be produced to a significantly larger extent. The question then is how to access **8**.

Scheme 2. Energy Profiles for Initiation Using H1 as Active Species[a]



[a] All zirconocenes shown are monocations; for clarity the charge is only indicated for **H1**. Values above straight reaction arrows denote the stability in internal energy *E* and Gibbs free energy *G* (*E*/*G*; kcal/mol) of the corresponding product relative to the reactant. Values above curved arrows denote the stability (*E*/*G*; kcal/mol) of the corresponding transition state relative to the reactant (the reaction of **H4** to **H5** is doubtful; cf. text).

If one thinks of the simple zirconocene hydride **9** (Scheme 3), it would be necessary to remove one of the two hydrides, which should be easily achieved by protonation. If $HNBu_3^+$ is the proton carrier, the desired reaction of $HNBu_3^+$ with **9** should lead to molecular hydrogen and the desired **8**. This reaction liberates energy of −6.71 kcal/mol (Scheme 4). However, free **9** could dimerize to form **10** during synthesis or upon dissolution in a solvent.[14a] $HNBu_3^+$ might not be able to cleave **10**, since this reaction is endothermic by +24.97 kcal/mol. $[\{Me_2Si(C_5Me_4)Zr(H)(\mu\text{-}H)\}_2]$ can be cleaved by donors such as THF or PMe_3,[10c] and so it was investigated if MVE would also be capable of achieving this with **10** (protonation could then be possible in the following step). Unfortunately, it turns out that the reaction of **10** with MVE to yield the corresponding **11** is strongly endothermic (+30.75 kcal/mol; Scheme 4). This means that in case **10** turns out to be unreactive an alternative must be found: a more appropriate complex would be one that carries a hydrogen on the zirconium center and a functional group or substituent which is present in a somewhat destabilized form in the complex. Upon protonation it would be released from the complex and react to the energetically more favorable form. Such a candidate might be **12** (which was chosen in analogy to $[\{Me_2Si(C_5Me_4)\}Zr(H)(Ph)]^{10c}$), bearing one hydrogen and one phenyl ring σ-bonded to the metal center. Protonation of this system yields the desired complex **8** if the phenyl ring is protonated selectively. From the energy profile it can

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(13) This molecule was chosen in analogy to the synthesis of $[\{Me_2C(Cp)_2\}Zr(Me)(thf)]^+$ out of $[\{Me_2C(Cp)_2\}Zr(Me)_2]$ and $HNBu_3BPh_4$, formally yielding $[\{Me_2C(Cp)_2\}Zr(Me)(NBu_3)][BPh_4]$, in which the NBu_3 ligand is replaced by THF that is present in the reaction mixture.[5] Here it is absolutely essential not to have any other strong donors—such as THF—present, because MVE cannot replace these at the metal center.

(14) (a) Syntheses of unbridged zirconocene hydrides such as $[Cp^*][CpMe]ZrH_2$ and $Cp^*_2ZrH_2$ by hydrogenation of $[Cp^*][CpMe]ZrMe_2$ and $Cp^*_2ZrMe_2$ were reported by Bercaw[14b] and Marks,[14c] respectively. However, the *ansa*-zirconocene complex $[\{Me_2Si(C_5Me_4)_2\}Zr(Me)_2]$ was shown by Desrosiers, Rheingold, and Parkin[10c] to be hydrogenated to $[\{Me_2Si(C_5Me_4)Zr(H)(\mu\text{-}H)\}_2]$ and $[\{Me_2Si(C_5Me_4)Zr(H)(Ph)]$, when the reaction is carried out in cyclohexane and benzene, respectively. In solution $[\{Me_2Si(C_5Me_4)Zr(H)(\mu\text{-}H)\}_2]$ dissociates to form $[\{Me_2Si(C_5Me_4)\}Zr(H)_2]$; however, at low temperatures the dimeric form is preferred (as it is in the crystal). These findings were explained by the higher Lewis acidity of the metal center compared to that of unbridged zirconocene hydrides with permethylated Cp rings (unbridged zirconocene hydrides with less heavily substituted Cp rings also tend to dimerize[15]). In our computationally studied system the Lewis acidity will be even higher than in the $Me_2Si(Cp^*)_2Zr$ fragment, since we utilize a Me_2C bridge which lowers the Cp−Zr−Cp angle even more. (b) Wolczanski, P. T.; Bercaw, J. E. *Organometallics* **1982**, *1*, 793−799. (c) Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701−7715. (d) A more detailed analysis of the potential of **9**, **10**, and **12** as precursors, of course, would have to include the determination of activation energies for the reactions mentioned in this subsection. This is postponed for furture work. The results mentioned here are meant to show experimentally promising trends for initiation.

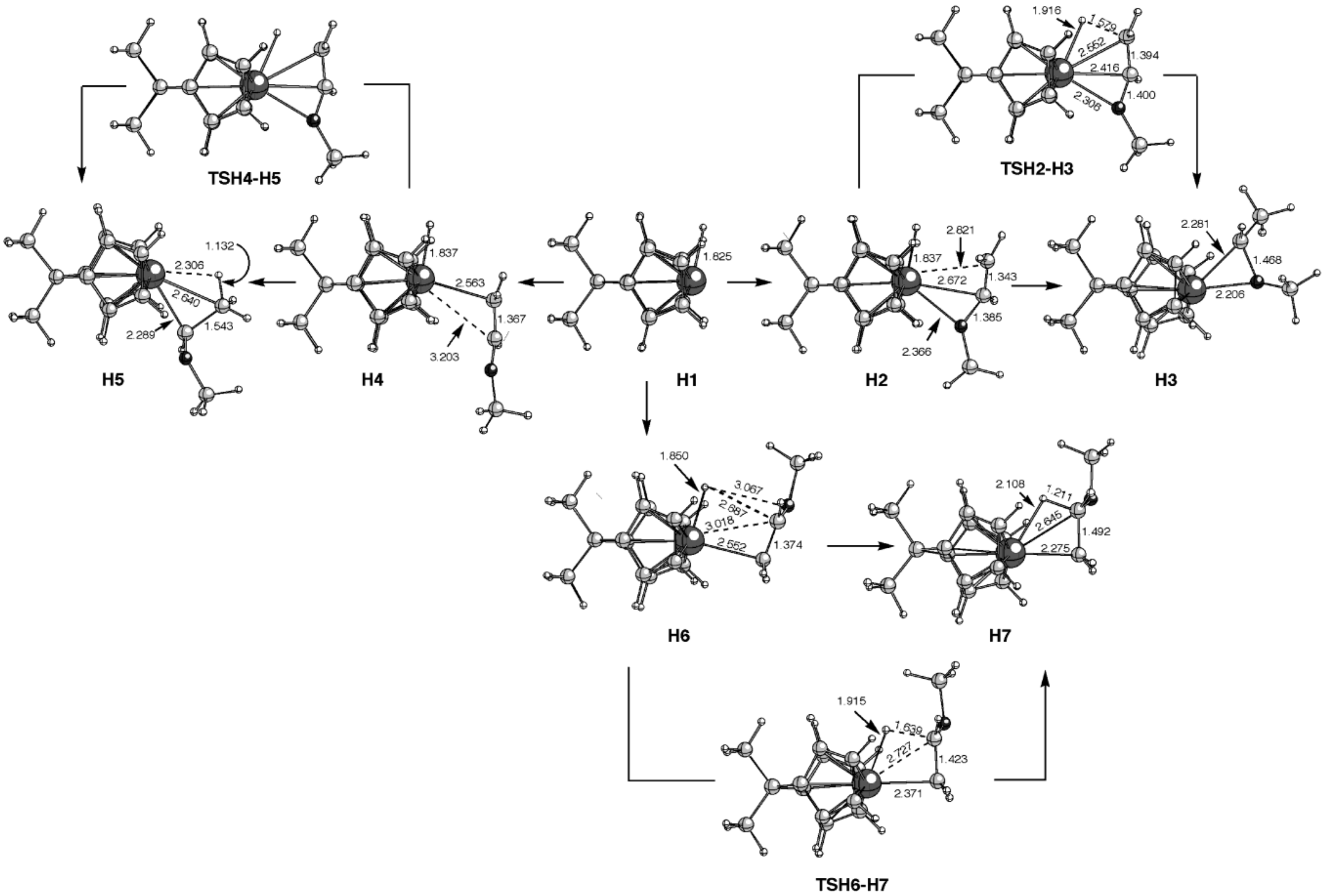
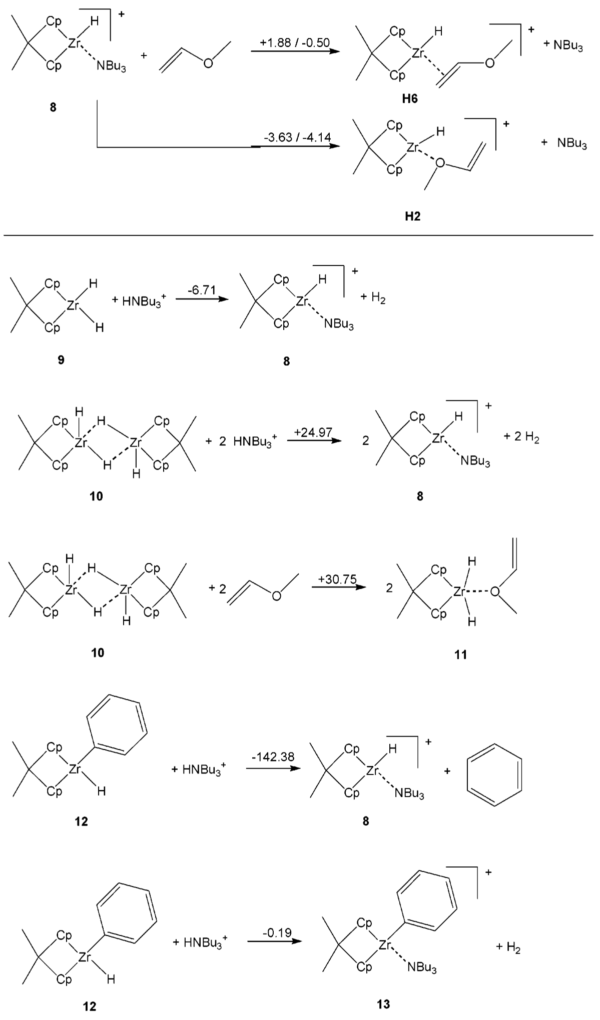


Figure 2. Calculated structures of molecules involved in the initiation via **H1** (atom distances in Å; atoms in decreasing size Zr, C, O, H).

Scheme 3. Energies *E* and Gibbs Free Energies *G* (*E*/*G*; kcal/mol) for Reactions Associated with Possible Catalyst Precursors



be concluded that chances to achieve this are good: upon formation of **8** and benzene −142.38 kcal/mol of energy is liberated, whereas the production of **13** and molecular hydrogen yields −0.19 kcal/mol. In case **9** cannot be generated without forming **10**, or if **10** will not react, **12** is worth a try.[14d]

Propagation and Possible Catalytic Cycles

Since the formation of **5** from **6** cannot be ruled out at this point (Scheme 1) and since the formation of **H3** is possible (Scheme 2), we continued the work with **5**. Again there should be three different chemical and regiochemical possibilities to add MVE to **5**: (i) coordination via the oxygen atom of the next MVE molecule, (ii) coordination via the olefinic double bond in the same orientation as in **3** (OMe group is oriented away from the Zr−C−O ring of **5**), and (iii) coordination via the olefinic double bond in reversed orientation.

Upon coordination of the second MVE molecule via the oxygen atom products **14**−**16** are formed (Scheme 4), which are more stable than the sum of the energies of **5** and MVE by −15.94, −15.62, and −20.89 kcal/mol, respectively (it was shown before that the coordination of an oxygen donor yields more stable products, when the central position in front of the zirconium center is also occupied by an oxygen atom).[16] Compounds **14** and **16** cannot react any further, since the reactive groups are too far away from each other. Also, **15** seems to be structurally unfavorable to react to give **19**, but to ensure this assumption, we looked for the transition state **TS15-19** and were not able to locate it. We therefore did not consider this sequence anymore. From these results it follows that upon coordinating the second MVE molecule via its oxygen atom, one ends up with compounds which cannot further contribute to the propagation reaction. Either these complexes are dead end roads or, more probably, they will dissociate and rearrange to other compounds which can react (vide infra).

The exothermicities upon formation of **17** and **18** (olefin coordination in both orientations) are very similar, liberating −16.69 and −17.95 kcal/mol of energy, respectively (Scheme 4, Figure 3). Thus, both compounds must be studied. **17** can react to give **19** (−21.59 kcal/mol) via the transition state **TS17-19** of moderately low energy (+15.12 kcal/mol). When the more loosely coordinated oxygen atom O1 in **19** is cleaved off and a new MVE molecule is added, the slightly endothermic product **26** (+1.70 kcal/mol) is formed. In an alternative coordination **28** can be formed, which is approximately as stable as **19** (−0.06 kcal/mol).

As an alternative, **18** can react to form **20** (−31.24 kcal/mol), and the energy of **TS18-20** is only +10.29 kcal/mol higher than the energy of **18**. Obviously, the five-membered ring (−Zr−O−C−C−C−) of **20** stabilizes the complex significantly. Upon cleavage of the coordinated oxygen in **20** and subsequent addition of the next MVE molecule products **21** and **22** are obtained, which are endothermic by +9.54 and +9.66 kcal/mol (again, very similar). Considerably more stable products such as **23**−**25** can be formed as intermediates (−9.97, −9.66, and −6.34 kcal/mol relative to **20**; cf. inserts in Scheme 4 and Figure 3) in going from **20** to **21** (**23**, **24**) and to **22** (**25**).

In this case it is noteworthy that the discussion would lead to a different result, when it is based on Gibbs free energies. As can be deduced from Scheme 4, the most stable product is **29**, which must give a compound such as **21** or **22** upon coordination of the next MVE molecule. However, this finally leads to a reaction with an overall endothermicity (vide infra). The only overall exothermic cycle would proceed via **17** → **19** → **26** → **27** → **17** etc.

The fundamental difference compared to polymerizations of ethylene, propylene, and MMA is that in the case of MVE there is a 1:1 chance that the olefinic double bond coordinates to the active center in one of the propagation steps or the oxygen atom of the ether group (in ethylene and propylene it is only the olefinic double bond and in MMA it is only the carbonyl oxygen, meaning that coordination is only possible via one functional group, which is clearly more straightforward than in the case of MVE). No matter which molecule of

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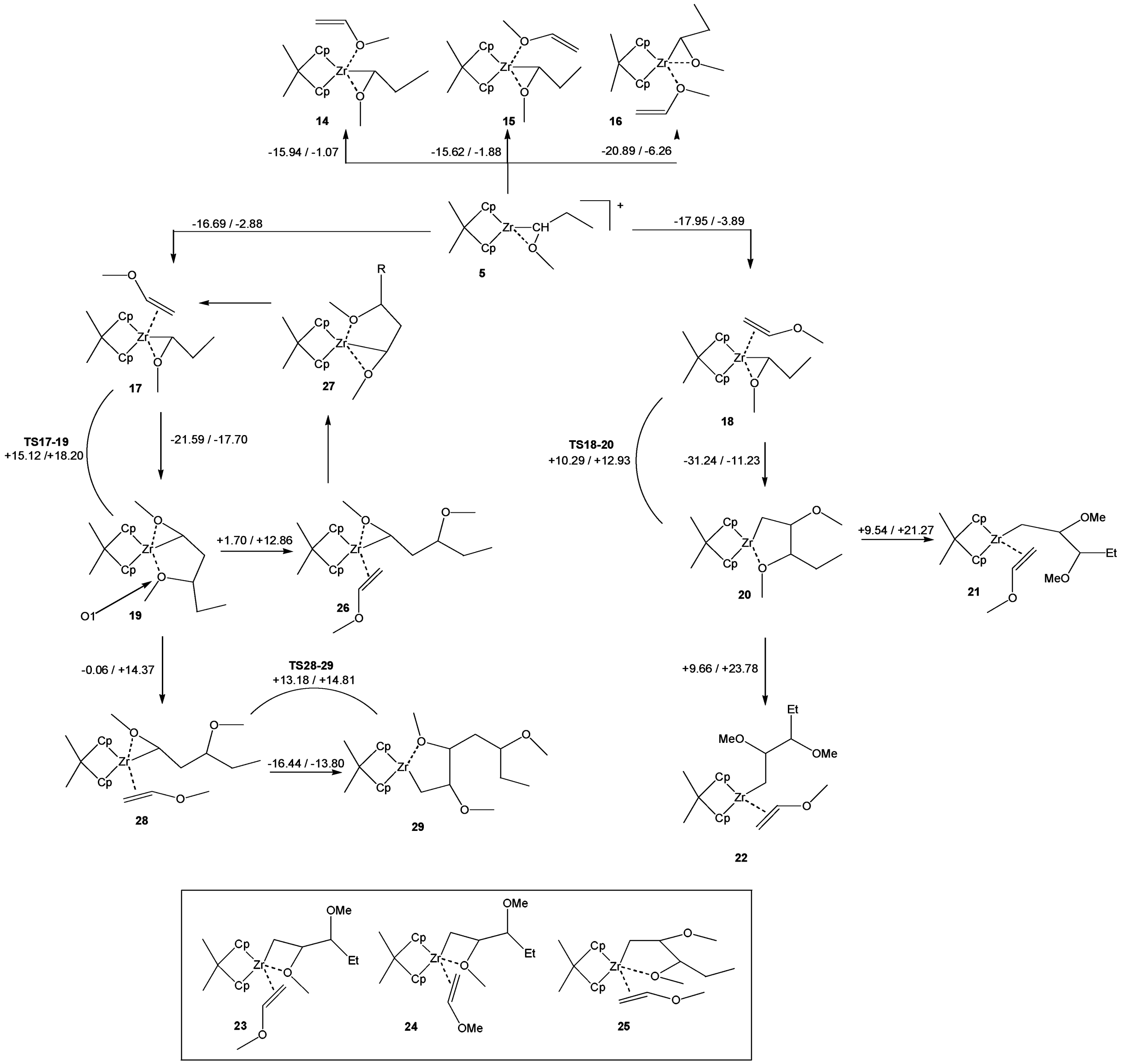
[15] (a) Jones, S. B.; Petersen, J. L. *Inorg. Chem.* **1981**, *20*, 2889−2894. (b) Choukroun, R.; Dahan, F.; Larsonneur, A.-M.; Samuel, E.; Petersen, J.; Meunier, P.; Sornay, C. *Organometallics* **1991**, *10*, 374−376. (c) Larsonneur, A.-M.; Choukroun, R.; Chaud, J. *Organometallics* **1993**, *12*, 3216−3224.

[16] Hölscher, M.; Keul, H.; Höcker, H. *Macromolecules* **2002**, *35*, 8194−8202.

Scheme 4. Energy Profiles for Propagation Using 5[a]



[a] All zirconocenes shown are monocations; for clarity the charge is only indicated for **5**. Values above straight reaction arrows denote the stability in internal energy *E* and Gibbs free energy *G* (*E*/*G*; kcal/mol) of the corresponding product relative to the reactant. Values above curved arrows denote the stability (*E*/*G*; kcal/mol) of the corresponding transition state relative to the reactant (the insert shows stable intermediates, which occur in the reaction of **20** to **21** or **22**).

the possible propagation steps is chosen (**21**, **22** or **26**, **28**), the MVE molecule to react now must coordinate via the olefinic double bond, which is the only possibility for the reaction to proceed (vide infra). If instead the oxygen atom of MVE coordinates to the metal center in one of these steps and not the C−C double bond, the reaction will not proceed any further due to structural reasons (reactive groups are too far away from each other and/or cannot come close enough; note for instance the impossibility of **15** to give **19**, vide supra). However, such coordination via oxygen can be broken, if the energy of the experimental system is high enough to allow for dissociation/reassociation, which means that over time the olefin can coordinate and react successfully. Whatever propagation step will be used, any following step will start from either **21**/**22** or **26**/**28**. In both cases we face a quasi-propylene-like situation. The major difference in **26** and **28** is an additional oxygen atom coordinating to the metal. Thus, we studied some of these reactions.

We assumed that the transformation of **26** to **27** (Scheme 4) will have approximately the same activation energy as the reaction of **17** to **19** (since it is electronically and structurally practically the same reaction), which prompted us not to calculate the step from **26** to **27**. For the time being, we assume that the reaction is possible and the activation energy amounts to ca. +15 kcal/mol.

The reaction of **28** to **29** is exothermic by −16.44 kcal/mol. The energy of **TS28-29** is higher by +13.18 kcal/mol than that of **28**. Thus, at this point there is no reason to believe that **27** or **29** would be preferred. Both

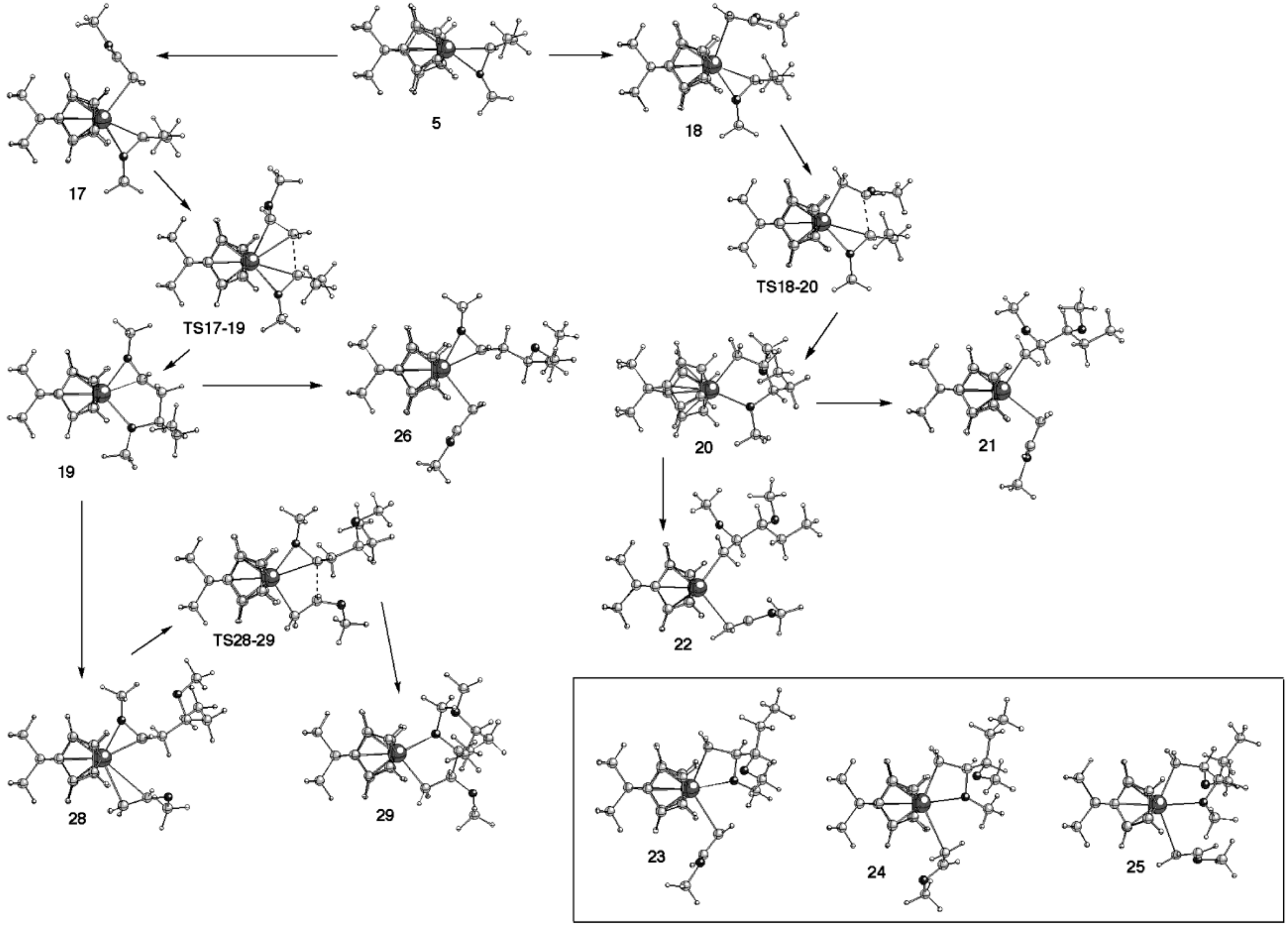
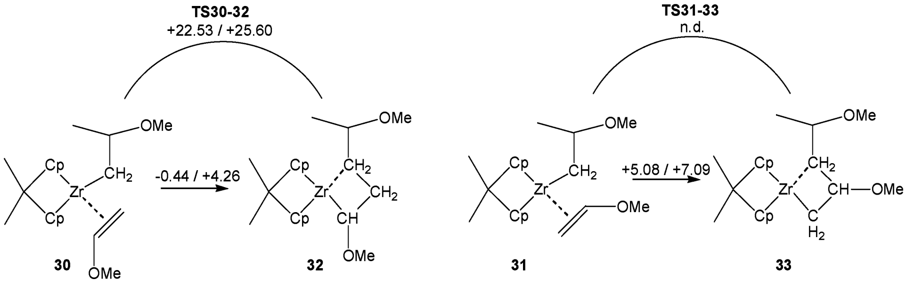


Figure 3. Calculated structures of molecules involved in the propagation via **5** (atoms in decreasing size Zr, C, O, H). The insert shows intermediates which can occur upon reaction from **20** to **21** and **22**; for details, see the text.

Scheme 5. Energy Profiles for Model Reactions of 30 to 32 and 31 to 33[a]



[a] Values above reaction arrows denote the stability in internal energy *E* and Gibbs free energy *G* (*E*/*G*; kcal/mol) of the corresponding product relative to the reactant. Values above curved arrows denote the stability (*E*/*G*; kcal/mol) of the corresponding transition state relative to the reactant.

reactions are possible, with activation energies in the range of ca. +15 kcal/mol.

In the next step we cut the growing chain of **21** and **22** to save some computation time by creating model compounds **30** and **31** (Scheme 5). We then located the corresponding products **32** and **33**, respectively. Interestingly, we found **32** to be only slightly more stable than **30** (−0.44 kcal/mol), but **33** is clearly an endothermic compound relative to **31** (+5.08 kcal/mol). Furthermore, it is striking that different from the hydride (**H6** → **H7**) but in accordance with the methyl transfer (**4** → **7**) no transition state could be located for the reaction of **31** to **33**. This again suggests such a sequence to be inoperative. We thus conclude that the only possible products during propagation are complexes such as **21**, **27**, and **29** but not **22** (**22** will form but cannot react further; the MVE molecule needs either to dissociate/recoordinate or rotate to generate an olefin coordination as in **21**). Interestingly, the activation energy for the reaction of **30** to **32** amounts to +22.53 kcal/mol and is therefore considerably higher compared to the activation energies for the reactions of **26** to **27** and **28** to **29**. This result is in accordance with 5-fold-coordinated zirconocene complexes being more stable than 4-fold-coordinated ones. However, on the basis of Gibbs free energies compound **32** would be the last point in an overall endothermic cycle, whereas the cycle leading to **27** can be considered exothermic. This means that on the basis of internal energies different active propagation channels are possible, whereas on the basis of Gibbs free energies only one active channel could be located. The location of unreactive products **14**, **15**, **16**, **29**, and **22** also reduces the chances to polymerize MVE with ease.

We note that the results presented will most certainly only be transferable to experiment when one uses a weakly coordinating counterion such as BPh_4^- and a single-component system. This is necessary, since it was shown by us and others before that the utilization of different counterions (such as perfluorotetraphenylborate) and the presence of other zirconocenes influences the polymerization mechanism heavily.[2a,5,17] In the case of MVE we assume that any anion which carries atoms or groups with electron lone pairs that are not needed in bonding within the anion (such as halogens, carbonyl oxygen, trivalent phosphorus compounds, etc.) will prevent polymerization due to blocking the metal center by strong coordination to it.

Summary

The general reaction steps of MVE polymerizations (initiation and propagation) using **1** and **H1** were elucidated by density functional calculations. The fundamental results are as follows. (i) Judging from all calculated activation energies and from the overall exothermicity of the reactions, polymerizations of this kind are possible, when internal energies are used for discussion. However, utilizing Gibbs free energies limits the possible reaction pathways to one propagation cycle and most likely to successful initiation only via **H1**. (ii) Unreactive yet stable products leading to dead reaction channels were also found. Since the formation of these products is reversible, the general possibility of polymerizing MVE is not affected, but chances for facile product formation are diminished. Unfortunately, theoretical studies of this kind cannot predict precise experimental conditions, but according to the activation energies obtained, somewhat elevated temperatures and prolonged reaction times seem to be necessary as well as noncoordinating anions and noncoordinating solvents.

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Supporting Information Available: A table giving values of *E*, E_{zpe}, and *G* and a figure giving the possibilities for the reaction of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Cameron, P. A.; Gibson, V. C.; Graham, A. J. *Macromolecules* **2000**, *33*, 4329−4335.